

第V欄 新規性、進歩性又は産業上の利用可能性についてのPCT規則43の2.1(a)(i)に定める見解、  
それを裏付ける文献及び説明

## 1. 見解

新規性 (N)	請求の範囲	1-15, 25-28	有 無
	請求の範囲	16-24	
進歩性 (IS)	請求の範囲	1-15, 25-28	有 無
	請求の範囲	16-24	
産業上の利用可能性 (IA)	請求の範囲	1-28	有 無
	請求の範囲		

## 2. 文献及び説明

文献1 : JP 2002-64097 A (株式会社東芝) 2002.02.28

文献2 : JP 2003-128820 A (大阪紡績株式会社) 2003.05.08

請求の範囲16-24に係る発明は国際調査報告で引用された文献1、2により新規性・進歩性を有しない。

## 理由

- ・請求の範囲16-19、21-24について

文献1にはシリコン基板をマイクロ波放電によるダウンフロープラズマにより活性化な弗素ガス処理することが記載されている。文献1発明で用いられるF2含有ガスと請求の範囲16-19、21-24の方法によるF2含有ガスとが相違するものとも認められない。

(文献1 : 特許請求の範囲, 【0076】 - 【0084】, 図5等参照)

- ・請求の範囲16-20について

文献2にはポリプロピレンを弗素ガス処理することが記載されている。文献2発明で用いられるF2含有ガスと請求の範囲16-19、21-24の方法によるF2含有ガスとが相違するものとも認められない。

(文献2 : 特許請求の範囲, 【0079】 - 【0084】, 図1等参照)

- ・請求の範囲1-15, 25-28について

請求の範囲1-16、25-28に係る発明は、国際調査報告に引用されたいずれの文献にも記載されておらず、また当業者にとって自明な事項でもない。



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EPO Customer Services

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Date

18.08.06

Reference	Application No./Patent No. 05727964.8 - 2111 PCT/JP2005006149
Applicant/Proprietor Kanto Denka Kogyo CO., LTD.	

#### Entry into the European phase before the European Patent Office

**These notes describe the procedural steps required for entry into the European phase before the European Patent Office (EPO). You are advised to read them carefully: failure to take the necessary action in time can lead to your application being deemed withdrawn.**

1. The above-mentioned international patent application has been given European application No. **05727964.8**.
2. Applicants **without** a residence or their principal place of business in an EPC contracting state may themselves initiate European processing of their international applications, provided they do so before expiry of the 31st month from the priority date (see also point 6 below).

**During the European phase before the EPO as designated or elected Office, however, such applicants must be represented by a professional representative (Arts. 133(2) and 134(1), (7) EPC).**

Procedural acts performed after expiry of the 31st month by a professional representative who acted during the international phase but is not authorised to act before the EPO have no legal effect and therefore lead to loss of rights.

**Please note that a professional representative authorised to act before the EPO and who acted for the applicant during the international phase does not automatically become the representative for the European phase. Applicants are therefore strongly advised to appoint in good time any representative they wish to initiate the European phase for them; otherwise, the EPO has to send all communications direct to the applicant.**

3. Applicants **with** a residence or their principal place of business in an EPC contracting state are not obliged to appoint, for the European phase before the EPO as designated or elected Office, a professional representative authorised to act before the EPO.  
**However, in view of the complexity of the procedure it is recommended that they do so.**
4. Applicants and professional representatives are also strongly advised to initiate the European phase using EPO Form 1200 (available free of charge from the EPO). This however is not compulsory.



5. **To enter the European phase before the EPO, the following acts must be performed.**  
(N.B.: Failure validly to do so will entail loss of rights or other adverse legal consequences.)

5.1 If the EPO is acting as **designated or elected Office** (Arts. 22(1)(3) and 39(1) PCT respectively), applicants must, within 31 months from the date of filing or (where applicable) the earliest priority date:

- a) Supply a translation of the international application into an EPO official language, if the International Bureau did not publish the application in such a language (Art. 22(1) PCT and R. 107(1)(a) EPC).  
**If the translation is not filed in time, the international application is deemed withdrawn before the EPO (R. 108(1) EPC).**  
This loss of rights is deemed not to have occurred if the translation is then filed within a two-month grace period as from notification of an EPO communication, provided a surcharge is paid at the same time (R. 108(3) EPC).
- b) Pay the national basic fee (EUR 170,00) and, where a supplementary European search report has to be drawn up, the search fee (EUR 720,00 ; R. 107(1)(c) and (e) EPC).
- c) If the time limit under Article 79(2) EPC expires before the 31-month time limit, pay the designation fee (EUR 80,00) for each contracting state designated (R. 107(1)(d) EPC).
- d) If the time limit under Article 94(2) EPC expires before the 31-month time limit, file the written request for examination and pay the examination fee (EUR 1490,00 ; R. 107(1)(f) EPC).
- e) Pay the third-year renewal fee (EUR 400,00) if it falls due before expiry of the 31-month time limit (R. 107(1)(g) EPC).

If the fees under (b) to (d) above are not paid in time, or the written request for examination is not filed in time, the international application is deemed withdrawn before the EPO, or the contracting-state designation(s) in question is (are) deemed withdrawn (R. 108(1) and (2) EPC). However, the fees may still be validly paid within a two-month grace period as from notification of an EPO communication, provided the necessary surcharges are paid at the same time (R. 108(3) EPC). For the renewal fee under (e) above, the grace period is six months from the fee's due date (Art. 86(2) EPC).

For an overview of search and examination fees, see OJ EPO 11/2005, 577 and 03/2006.

5.2 If the application documents on which the European grant procedure is to be based comprise more than ten claims, a claims fee is payable within the 31-month time limit under Rule 107(1) EPC for the eleventh and each subsequent claim (R. 110(1) EPC). The fee can however still be paid within a one-month grace period as from notification of an EPO communication pointing out the failure to pay (R. 110(2) EPC).

6. If the applicant had a representative during the application's international phase, the present notes will be sent to the representative, asking him to inform the applicant accordingly.

**All subsequent communications will be sent to the applicant, or - if the EPO is informed of his appointment in time - to the applicant's European representative.**



Date

Sheet 3

Application No. 05727964.8

7. For more details about time limits and procedural acts before the EPO as designated and elected Office, see the EPO brochure

How to get a European patent  
Guide for applicants - Part 2  
PCT procedure before the EPO - "Euro-PCT"

This brochure, the list of professional representatives before the EPO, Form 1200 and details of the latest fees are now all available on the Internet under

<http://www.european-patent-office.org>

Receiving section



13. Juli 2006

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An das Europäische Patentamt  
Nur für ab 1. Juli 1999 eingereichte  
internationale Anmeldungen!

Eintritt in die  
europäische Phase vor dem  
(EPA als Bestimmungsamt  
oder ausgewähltes Amt)

To the European Patent Office  
Only for international applications filed from  
1 July 1999 onwards!

Entry into the  
European phase  
(EPO as designated or  
elected Office)

A l'office européen des brevets  
Seulement pour les demandes internationa-  
les déposées à compter du 1er juillet 1999!

Entrée dans la  
phase européenne  
(l'OEB agissant en qualité  
d'office désigné ou élu)

Europäische Anmeldenummer oder, falls nicht bekannt, PCT-Aktenzeichen oder PCT-Veröffentlichungsnummer	European application number, or, if not known, PCT application or publication number <b>05 727 964.8    WO 2005/095268 A1</b>	Numéro de dépôt de la demande de brevet européen ou, à défaut numéro de dépôt PCT ou de publication PCT
Zeichen des Anmelders oder Vertreters (max. 15 Positionen)	Applicant's or representative's reference (max. 15 spaces) <b>069EP 1009 SE</b>	Référence du demandeur ou du mandataire (15 caractères ou espaces au maximum)
<input checked="" type="checkbox"/> <b>1. Anmelder</b> Die Angaben über den (die) Anmelder sind in der internationalen Veröffentlichung enthalten oder vom Internationalen Büro nach der internationalen Veröffentlichung vermerkt werden.  <input type="checkbox"/> Änderungen, die das Internationale Büro noch nicht vermerkt hat, sind auf einem Zusatzblatt angegeben.  Zustellanschrift (siehe Merkblatt II, 1)	<b>1. Applicant</b> Indications concerning the applicant(s) are contained in the international publication or recorded by the International Bureau after the international publication.  Changes which have not yet been recorded by the International Bureau are set out on an additional sheet.  Address for correspondence (see Notes II, 1)	<b>1. Demandeur</b> Les indications concernant le(s) demandeur(s) figurent dans la publication internationale ou ont été enregistrées par le Bureau international après la publication internationale.  Les changements qui n'ont pas encore été enregistrés par le Bureau international sont indiqués sur une feuille additionnelle.  Adresse pour la correspondance (voir notice II, 1)
<b>Zur Kasse S. € 3.7M,-</b>		
<b>2. Vertreter</b>  Name (Nur einen Vertreter angeben, der in das europäische Patentregister eingetragen und an den zugestellt wird) Geschäftsanschrift   Telefon  Telefax                      Telex  <input type="checkbox"/> Weitere(r) Vertreter auf Zusatzblatt	<b>2. Representative</b>  Name (Name only one representative who is to be listed in the Register of European Patents and to whom notification is to be made) Address of place of business <b>PFENNING, MEINIG &amp; PARTNER GbR</b>  Theresienhöhe 13 D-80339 München  Telephone <b>+49 89 5309336</b>  Fax                              Telex <b>+49 89 532229</b>  Additional representative(s) on additional sheet	<b>2. Mandataire</b>  Nom (N'indiquer qu'un seul mandataire, qui sera inscrit au Registre européen des brevets et auquel signification sera faite)  Adresse professionnelle   Téléphone  Téléfax                      Télex  Autre(s) mandataire(s) sur une feuille additionnelle
<b>3. Vollmacht</b>  <input type="checkbox"/> Einzelvollmacht ist beigelegt.  <input type="checkbox"/> Allgemeine Vollmacht ist registriert unter Nummer:    <input type="checkbox"/> Allgemeine Vollmacht ist eingereicht, aber noch nicht registriert.  <input type="checkbox"/> Die beim EPA als PCT-Anmeldeamt eingereichte Vollmacht schließt ausdrücklich die regionale Phase ein.	<b>3. Authorisation</b>  Individual authorisation is attached.  General authorisation has been registered under No:    A general authorisation has been filed, but not yet registered.  The authorisation filed with the EPO as PCT receiving Office expressly includes the regional phase.	<b>3. Pouvoir</b>  Un pouvoir spécial est joint.  Un pouvoir général a été enregistré sous le n°:    Un pouvoir général a été déposé, mais n'est pas encore enregistré.  Le pouvoir général déposé à l'OEB agissant en qualité d'office récepteur au titre du PCT s'applique expressément à la phase régionale.

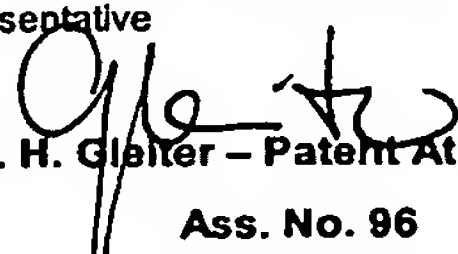
<input checked="" type="checkbox"/> 4. <b>Prüfungsantrag</b> Hiermit wird die Prüfung der Anmeldung gemäß Art. 94 EPÜ beantragt. Die Prüfungsgebühr wird (wurde) entrichtet.  <i>Prüfungsantrag in einer zugelassenen Nichtamtssprache (siehe Merkblatt III, 5.2):</i>	4. <b>Request for examination</b> Examination of the application under Art. 94 EPC is hereby requested. The examination fee is being (has been, will be) paid.  <i>Request for examination in an admissible non-EPO language (see Notes III, 5.2):</i>	4. <b>Requête en examen</b> Il est demandé que soit examinée la demande de brevet, conformément à l'art. 94 CBE. Il est (a été, sera) procédé au paiement de la taxe d'examen.  <i>Requête en examen dans une langue non officielle autorisée (voir notice III, 5.2):</i>
<input checked="" type="checkbox"/> 5. <b>Abschriften</b> Zusätzliche Abschrift(en) der im ergänzenden europäischen Recherchenbericht angeführten Schriftstücke wird (werden) beantragt.  Anzahl der zusätzlichen Sätze von Abschriften	5. <b>Copies</b> Additional copy (copies) of the documents cited in the supplementary European search report is (are) requested.  Number of additional sets of copies  One	5. <b>Copies</b> Prière de fournir une ou plusieurs copie supplémentaire des documents cités dans le rapport complémentaire de recherche européenne.  Nombre de jeux supplémentaires de copies
6. <b>Für das Verfahren vor dem EPA bestimmte Unterlagen</b>  6.1 Dem Verfahren vor dem EPA als Bestimmungsamt (PCT I) sind folgende Unterlagen zugrunde zu legen:  <input checked="" type="checkbox"/> die vom Internationalen Büro veröffentlichten Anmeldungsunterlagen (mit allen Ansprüchen, Beschreibung und Zeichnungen), gegebenenfalls mit den geänderten Ansprüchen nach Art. 19 PCT  <input checked="" type="checkbox"/> soweit sie nicht ersetzt werden durch die beigefügten Änderungen.  <i>Falls nötig, sind Klarstellungen auf einem Zusatzblatt einzureichen!</i>  6.2 Dem Verfahren vor dem EPA als ausgewähltem Amt (PCT II) sind folgende Unterlagen zugrunde zu legen:  <input type="checkbox"/> die dem Internationalen vorläufigen Prüfungsbericht zugrunde gelegten Unterlagen einschließlich seiner eventuellen Anlagen (Solche Anlagen müssen immer beigefügt werden)  <input type="checkbox"/> soweit sie nicht ersetzt werden durch die beigefügten Änderungen.  <i>Falls nötig, sind Klarstellungen auf einem Zusatzblatt einzureichen!</i>  <input type="checkbox"/> Sind dem EPA als mit der internationalen vorläufigen Prüfung beauftragten Behörde Versuchsberichte zugegangen, dürfen diese dem Verfahren vor dem EPA zugrunde gelegt werden.	6. <b>Documents intended for proceedings before the EPO</b>  6.1 Proceedings before the EPO as designated Office (PCT I) are to be based on the following documents:  the application documents published by the International Bureau (with all claims, description and drawings), where applicable with amended claims under Art. 19 PCT  unless replaced by the amendments enclosed.  <i>Where necessary, clarifications must be submitted on a separate sheet!</i>  6.2 Proceedings before the EPO as elected Office (PCT II) are to be based on the following documents:  the documents on which the international preliminary examination report is based, including its possible annexes (Such annexes must always be filed)  unless replaced by the amendments enclosed.  <i>Where necessary, clarifications must be submitted on a separate sheet!</i>  If the EPO as International Preliminary Examining Authority has received test reports, these may be used as the basis of proceedings before the EPO.	6. <b>Pièces destinées à la procédure devant l'OEB</b>  6.1 La procédure devant l'OEB agissant en qualité d'office désigné (PCT I) doit se fonder sur les pièces suivantes:  les pièces de la demande publiée par le Bureau international (avec toutes les revendications, la description et les dessins), éventuellement avec les revendications modifiées conformément à l'article 19 du PCT  dans la mesure où elles ne sont pas remplacées par les modifications jointes.  <i>Le cas échéant, des explications doivent être jointes sur une feuille additionnelle!</i>  6.2 La procédure devant l'OEB agissant en qualité d'office élu (PCT II) doit se fonder sur les pièces suivantes:  les pièces sur lesquelles se fonde le rapport d'examen préliminaire international, y compris ses annexes éventuelles (De telles annexes sont toujours à joindre)  dans la mesure où elles ne sont pas remplacées par les modifications jointes.  <i>Le cas échéant, des explications doivent être jointes sur une feuille additionnelle!</i>  Si l'OEB, agissant en qualité d'administration chargée de l'examen préliminaire international, a reçu des rapports d'essais, ceux-ci peuvent constituer la base de la procédure devant l'OEB.



<p><b>7. Übersetzungen</b> Beigefügt sind die nachfolgend angekreuzten Übersetzungen in einer der Amtssprachen des EPA (Deutsch, Englisch, Französisch):</p> <ul style="list-style-type: none"> <li><input checked="" type="checkbox"/> <i>Im Verfahren vor dem EPA als Bestimmungsamt oder ausgewähltem Amt (PCT I+II):</i> Übersetzung der ursprünglich eingereichten Internationalen Anmeldung (Beschreibung, Ansprüche, etwaige Textbestandteile in den Zeichnungen), der veröffentlichten Zusammenfassung, und etwaiger Angaben über biologisches Material nach Regel 13<sup>bb</sup>.3 und 13<sup>bb</sup>.4 PCT</li> <li><input type="checkbox"/> Übersetzung der prioritätsbegründenden Anmeldung(en)</li> <li><input type="checkbox"/> Es wird hiermit erklärt, daß die internationale Anmeldung in ihrer ursprünglich eingereichten Fassung eine vollständige Übersetzung der früheren Anmeldung ist (Regel 38(5) EPÜ)</li> <li><input type="checkbox"/> <i>Zusätzlich im Verfahren vor dem EPA als Bestimmungsamt (PCT I):</i> Übersetzung der nach Art. 19 PCT geänderten Ansprüche nebst Erklärung, falls diese dem Verfahren vor dem EPA zugrunde gelegt werden sollen (siehe Feld 6)</li> <li><input type="checkbox"/> <i>Zusätzlich im Verfahren vor dem EPA als ausgewähltem Amt (PCT II):</i> Übersetzung der Anlagen zum Internationalen vorläufigen Prüfungsbericht</li> </ul>	<p><b>7. Translations</b> Translations in one of the official languages of the EPO (English, French, German) are enclosed as crossed below:</p> <ul style="list-style-type: none"> <li><i>In proceedings before the EPO as designated or elected Office (PCT I + II):</i> Translation of the International application (description, claims, any text in the drawings) as originally filed, of the abstract as published and of any indication under Rule 13<sup>bb</sup>.3 and 13<sup>bb</sup>.4 PCT regarding biological material</li> <li>Translation of the priority application(s): To follow</li> <li>It is hereby declared that the international application as originally filed is a complete translation of the previous application (Rule 38(5) EPC)</li> <li><i>In addition, in proceedings before the EPO as designated Office (PCT I):</i> Translation of amended claims and any statement under Art. 19 PCT, if the claims as amended are to form the basis for the proceedings before the EPO (see Section 6)</li> <li><i>In addition, in proceedings before the EPO as elected office (PCT II):</i> Translation of any annexes to the International preliminary examination report</li> </ul>	<p><b>7. Traductions</b> Vous trouverez ci-jointes les traductions cochées ci-après dans l'une des langues officielles de l'OEB (allemand, anglais, français):</p> <ul style="list-style-type: none"> <li><i>Dans la procédure devant l'OEB agissant en qualité d'office désigné ou élu (PCT I + II):</i> Traduction de la demande internationale telle que déposée initialement (description, revendications, textes figurant éventuellement dans les dessins), de l'abrégé publié, et de toutes indications visées aux règles 13<sup>bb</sup>.3 et 13<sup>bb</sup>.4 du PCT concernant le matériel biologique</li> <li>Traduction de la (des) demande(s) ouvrant le droit de priorité</li> <li>Il est déclaré par la présente que la demande internationale telle que déposée initialement est une traduction intégrale de la demande antérieure (règle 38(5) CBE)</li> <li><i>De plus, dans la procédure devant l'OEB agissant en qualité d'office désigné (PCT I):</i> Traduction des revendications modifiées et de la déclaration faite conformément à l'article 19 du PCT, si la procédure devant l'OEB doit être fondée sur les revendications modifiées (voir la rubrique 6)</li> <li><i>De plus, dans la procédure devant l'OEB agissant en qualité d'office élu (PCT II):</i> Traduction des annexes du rapport d'examen préliminaire international</li> </ul>
<p><b>8. Biologisches Material</b> Die Erfindung bezieht sich auf bzw. verwendet biologisches Material, das nach Regel 28 EPÜ hinterlegt worden ist.</p> <p><input type="checkbox"/> Die Angaben nach Regel 28(1)(c) EPÜ (falls noch nicht bekannt, die Hinterlegungsstelle und das (die) Bezugszeichen [Nummer, Symbole usw.] des Hinterlegers) sind in der internationalen Veröffentlichung oder in der gemäß Feld 7 eingereichten Übersetzung enthalten auf:</p> <p>Seite(n) / Zeile(n)</p> <p>Die Empfangsbescheinigung(en) der Hinterlegungsstelle</p> <p><input type="checkbox"/> ist (sind) beigefügt</p> <p><input type="checkbox"/> wird (werden) nachgereicht</p> <p><input type="checkbox"/> Verzicht auf die Verpflichtung des Antragstellers nach Regel 28(3) auf gesondertem Schriftstück</p>	<p><b>8. Biological material</b> The invention relates to and/or uses biological material deposited under Rule 28 EPC.</p> <p>The particulars referred to in Rule 28(1)(c) EPC (if not yet known, the depository institution and the identification references(s) [number, symbols, etc.] of the depositor) are given in the international publication or in the translation submitted under Section 7 on:</p> <p>page(s) / line(s)</p> <p>The receipt(s) of deposit issued by the depository institution</p> <p>is (are) enclosed</p> <p>will be filed at a later date</p> <p>Waiver of the right to an undertaking from the requester pursuant to Rule 28(3) attached.</p>	<p><b>8. Matière biologique</b> L'invention concerne et/ou utilise la matière biologique, déposée conformément à la règle 28 CBE.</p> <p>Les indications visées à la règle 28(1)(c) CBE (si pas encore connues, l'autorité de dépôt et la (les) référence(s) d'identification [numéro ou symboles etc.] du déposant) figurent dans la publication internationale ou dans une traduction produite conformément à la rubrique 7 à la / aux:</p> <p>page(s) / ligne(s)</p> <p>Le(s) récépissé(s) de dépôt délivré(s) par l'autorité de dépôt</p> <p>est (sont) joint(s)</p> <p>sera (seront) produit(s) ultérieurement</p> <p>Renonciation, sur document distinct, à l'engagement du requérant au titre de la règle 28(3).</p>

<p><b>9. Nucleotid- und Aminosäuresequenzen</b></p> <p><input type="checkbox"/> Die nach Regeln 5.2 und 13<sup>ter</sup> PCT sowie Regel 111(3) EPÜ erforderlichen Unterlagen liegen dem EPA bereits vor.</p> <p><input type="checkbox"/> Das schriftliche Sequenzprotokoll wird anliegend in einer Amtssprache des EPA nachgereicht.</p> <p><input type="checkbox"/> Das Sequenzprotokoll geht nicht über den Inhalt der Anmeldung in der ursprünglich eingereichten Fassung hinaus.</p> <p><input type="checkbox"/> Der vorgeschriebene maschinenlesbare Datenträger ist beigelegt.</p> <p><input type="checkbox"/> Die auf dem Datenträger gespeicherte Information stimmt mit dem schriftlichen Sequenzprotokoll überein.</p>	<p><b>9. Nucleotide and amino acid sequences</b></p> <p>The items necessary in accordance with Rules 5.2 and 13<sup>ter</sup> PCT and Rule 111(3) EPC have already been furnished to the EPO.</p> <p>The written sequence listing is furnished herewith in an official language of the EPO.</p> <p>The sequence listing does not include matter which goes beyond the content of the application as filed.</p> <p>The prescribed machine-readable data carrier is enclosed.</p> <p>The information recorded on the data carrier is identical to the written sequence listing.</p>	<p><b>9. Séquences de nucléotides et d'acides aminés</b></p> <p>Les pièces requises selon les règles 5.2 et 13<sup>ter</sup> PCT et la règle 111(3) CBE ont déjà été déposées auprès de l'OEB.</p> <p>La liste de séquences écrite est produite ci-joint dans une des langues officielles de l'OEB.</p> <p>La liste de séquences ne contient pas d'éléments s'étendant au-delà du contenu de la demande telle qu'elle a été déposée.</p> <p>Le support de données prescrit, déchiffirable par machine, est annexé.</p> <p>L'information figurant sur le support de données est identique à celle que contient la liste de séquences écrite.</p>
<p><b>10. Benennungsgebühren *</b></p> <p><input type="checkbox"/> 10.1 Es ist derzeit beabsichtigt, den siebenfachen Betrag einer Benennungsgebühr zu entrichten. Damit gelten die Benennungsgebühren für alle Vertragsstaaten des EPÜ<sup>1</sup> als entrichtet (Art. 2 Nr. 3 GebO), soweit sie in der internationalen Anmeldung bestimmt sind.</p> <p><input checked="" type="checkbox"/> 10.2 Abweichend von der Erklärung in Nr. 10.1 ist derzeit beabsichtigt, weniger als sieben Benennungsgebühren für folgende in der internationalen Anmeldung bestimmte Vertragsstaaten des EPÜ<sup>2</sup> zu entrichten:</p> <p>(1) <u>DE</u> GERMANY</p> <p>(2) <u>FR</u> FRANCE</p> <p>(3) <u>GB</u> UNITED KINGDOM</p>	<p><b>10. Designation fees *</b></p> <p>10.1 It is currently intended to pay seven times the amount of the designation fee. The designation fees for all the EPC contracting states<sup>1</sup> designated in the international application are thereby deemed to have been paid (Art. 2 No. 3 RFees).</p> <p>10.2 The declaration in No. 10.1 does not apply. Instead, it is currently intended to pay fewer than seven designation fees for the following EPC contracting states<sup>2</sup> designated in the international application:</p> <p>(4) <u>    </u></p> <p>(5) <u>    </u></p> <p>(6) <u>    </u></p>	<p><b>10. Taxes de désignation *</b></p> <p>10.1 Il est actuellement envisagé de payer un montant correspondant à sept fois la taxe de désignation. Les taxes de désignation sont ainsi réputées payées pour tous les Etats contractants de la CBE<sup>1</sup> désignés dans la demande internationale (art. 2, point 3 du RRT).</p> <p>10.2 Contrairement à ce qui est indiqué au n° 10.1, il est actuellement envisagé de payer moins de sept taxes de désignation pour les Etats contractants de la CBE<sup>2</sup> suivants désignés dans la demande internationale:</p>
<p>Soweit unter Nr. 10.2 Vertragsstaaten aufgeführt sind, wird beantragt, für die dort nicht angeführten Vertragsstaaten von der Zustellung einer Mitteilung nach Regel 108(3) EPÜ abzusehen.</p> <p><input type="checkbox"/> 10.3 Wird ein automatischer Abbuchungsauftrag erteilt (Feld 12), so wird das EPA beauftragt, bei Ablauf der Grundfrist nach Regel 107(1)d) EPÜ den siebenfachen Betrag einer Benennungsgebühr abzubuchen. Ist eine Erklärung nach Nr. 10.2 abgegeben worden, so sollen die Benennungsgebühren nur für die dort angegebenen Vertragsstaaten abgebucht werden, sofern dem EPA nicht bis zum Ablauf der Grundfrist ein anderslautender Auftrag zugeht.</p>	<p>If contracting states are indicated under No. 10.2, it is requested that no communication under Rule 108(3) EPC be issued for contracting states not thus indicated.</p> <p>10.3 If an automatic debit order has been issued (Section 12), the EPO is authorised, on expiry of the basic period under Rule 107(1)(d) EPC, to debit seven times the amount of the designation fee. If states are indicated under No. 10.2, the EPO will debit designation fees only for those states, unless instructed otherwise before the basic period expires.</p>	<p>Si des états contractants sont mentionnés au n°. 10.2, prière de ne pas procéder à la signification d'une notification prévue par la règle 108(3) CBE pour les Etats contractants n'y ayant pas été mentionnés.</p> <p>10.3 Si un ordre de prélèvement automatique est donné (rubrique 12), il est demandé à l'OEB de prélever, à l'expiration du délai normal visé à la règle 107(1)d) CBE, un montant correspondant à sept fois la taxe de désignation. Si une déclaration a été faite au n° 10.2, les taxes de désignation ne sont à prélever que pour les Etats contractants qui y sont indiqués, sauf instruction contraire reçue par l'OEB avant l'expiration du délai normal.</p>
<p>* Form 1200 (01.02) nur verwendet für internationale Anmeldungen, die ab 1. Juli 1999 eingereicht worden sind.</p> <p>1 Stand bei Drucklegung: 20 Vertragsstaaten, und zwar: / Status when this form was printed: 20 contracting states, namely / Situation à la date d'impression: 20 Etats contractants, à savoir: AT Österreich / Austria / Autriche, BE Belgien / Belgium / Belgique, CH/LI Schweiz und Liechtenstein / Switzerland and Liechtenstein / Suisse et Liechtenstein, CY Zypern / Cyprus / Chypre, DE Deutschland / Germany / Allemagne, DK Dänemark / Denmark / Danemark, ES Spanien / Spain / Espagne, FI Finnland / Finland / Finlande, FR Frankreich / France / France, GB Vereinigtes Königreich / United Kingdom / Royaume-Uni, GR Griechenland / Greece / Grèce, IE Irland / Ireland / Irlande, IT Italien / Italy / Italie, LU Luxemburg / Luxembourg / Luxembourg, MC Monaco / Monaco / Monaco, NL Niederlande / Netherlands / Pays-Bas, PT Portugal / Portugal / Portugal, SE Schweden / Sweden / Suède, TR Türkei / Turkey / Turquie</p> <p>2 Für Türkei nur möglich, falls in der internationalen Anmeldung am oder nach dem 1. November 2000 bestimmt. / For Turkey possible only if designated in the international application on or after 1 November 2000. / En ce qui concerne Turquie, seulement si la désignation a été effectuée dans la demande internationale le 1er novembre 2000 ou à une date ultérieure.</p>	<p>* Use Form 1200 (01.02) only for international applications filed from 1 July 1999 onwards.</p>	<p>* Veuillez utiliser le formulaire 1200 (01.02) seulement pour les demandes internationales déposées à compter du 1<sup>er</sup> juillet 1999.</p>



<input type="checkbox"/> <b>11. Erstreckung des europäischen Patents</b> Diese Anmeldung gilt auch als Erstreckungsantrag für alle in der internationalen Anmeldung bestimmten Nicht-Vertragsstaaten des EPÜ, mit denen bei Einreichung der internationalen Anmeldung »Erstreckungsabkommen« in Kraft waren. Die Erstreckung wird jedoch nur wirksam, wenn die vorgeschriebene Erstreckungsgebühr entrichtet wird. Es wird derzeit beabsichtigt, die Erstreckungsgebühr für die nachfolgend angekreuzten Staaten zu entrichten:  <input type="checkbox"/> SI Slowenien <input type="checkbox"/> LT Litauen <input type="checkbox"/> LV Lettland <input type="checkbox"/> AL Albanien <input type="checkbox"/> RO Rumänien <input type="checkbox"/> MK Ehemalige jugoslawische Republik Mazedonien  <input type="checkbox"/> _____ 1)	<b>11. Extension of the European patent</b>  This application is also considered as being a request for extension to all the non-Contracting States to the EPC designated in the International application with which "extension agreements" were in force on the date of filing the international application. However, the extension only takes effect if the prescribed extension fee is paid. It is currently intended to pay the extension fee for the States marked with a cross below:  Slovenia Lithuania Latvia Albania Romania Former Yugoslav Republic of Macedonia  <input type="checkbox"/> _____ 1)	<b>11. Extension des effets du brevet européen</b> La présente demande est également réputée demande d'extension à tous les Etats non contractants de la CBE désignés dans la demande internationale, avec lesquels existaient, lors du dépôt de la demande, des «accords d'extension». Toutefois l'extension ne produit ses effets que si la taxe d'extension prescrite est acquittée. Il est actuellement envisagé de payer la taxe d'extension pour les Etats dont le nom est coché ci-après:  Slovénie Lituanie Lettonie Albanie Roumanie Ex-République yougoslave de Macédoine  <input type="checkbox"/> _____ 1)
<input type="checkbox"/> <b>12. Automatischer Abbuchungsauftrag (Nur möglich für Inhaber von beim EPA geführten laufenden Konten)</b>  Das EPA wird beauftragt, nach Maßgabe der Vorschriften über das automatische Abbuchungsverfahren fällige Gebühren und Auslagen vom entstehenden laufenden Konto abzubuchen. Im Bezug auf die Benennungsgebühren wird auf Feld 10.3 verwiesen. Das EPA wird ferner beauftragt, die Erstreckungsgebühren für jeden in Feld 11 angekreuzten »Erstreckungsstaat« bei Ablauf der Grundfrist zu ihrer Zahlung abzubuchen, sofern ihm nicht bis dahin ein anderslautender Auftrag zugeht.  Nummer und Kontoinhaber _____	<b>12. Automatic debit order (for EPO deposit account holders only)</b>  The EPO is hereby authorised, under the Arrangements for the automatic debiting procedure, to debit from the deposit account below any fees and costs falling due. For designation fees, see Section 10.3. The EPO is also authorised, on expiry of the basic period for paying the extension fees, to debit those fees for each of the "extension states" marked with a cross in Section 11, unless instructed otherwise before the said period expires.  Number and account holder _____	<b>12. Ordre de prélèvement automatique (uniquement possible pour les titulaires de comptes courants ouverts auprès de l'OEB)</b> Par la présente, il est demandé à l'OEB de prélever du compte courant ci-dessous les taxes et frais venant à échéance, conformément à la réglementation relative au prélèvement automatique. Pour les taxes de désignation, se reporter à la rubrique 10.3. Il est en outre demandé à l'OEB de prélever, à l'expiration du délai normal prévu pour leur paiement, les taxes d'extension pour chaque « Etat autorisant l'extension » coché à la rubrique 11, sauf instruction contraire reçue avant l'expiration de ce délai.  Numéro et titulaire du compte _____
<input type="checkbox"/> <b>13. Eventuelle Rückzahlungen auf das beim EPA geführte laufende Konto</b> Nummer und Kontoinhaber _____	<b>13. Any reimbursement to EPO deposit account</b> Number and account holder _____	<b>13. Remboursements éventuels à effectuer sur le compte courant ouvert auprès de l'OEB</b> Numéro et titulaire du compte _____
<b>14. Unterschrift(en) des (der) Anmelder(s) oder Vertreters</b>  Ort / Datum Für Angestellte (Art. 133(3) EPÜ) mit allgemeiner Vollmacht: Nr. _____  Name(n) des (der) Unterzeichneten bitte in Druckschrift wiederholen. Bei juristischen Personen bitte auch die Stellung des (der) Unterzeichneten innerhalb der Gesellschaft in Druckschrift angeben.	<b>14. Signature(s) of applicant(s) or representative</b>   Dr. H. Glaser – Patent Attorney Ass. No. 96  Place / Date Munich, July 10, 2006 For employees (Art. 133(3) EPC) having a general authorisation: No. _____  Please print name(s) under signature(s). In the case of legal persons, the position of the signatory within the company should also be printed.	<b>14. Signature(s) du (des) demandeur(s) ou du mandataire</b>  Lieu / Date Pour les employés (art. 133(3) CBE) disposant d'un pouvoir général: N° _____  Le ou les noms des signataires doivent être indiqués en caractères d'imprimerie. S'il s'agit d'une personne morale, la position occupée au sein de celle-ci par le ou les signataires doit également être indiquée en caractères d'imprimerie.

SPECIFICATION

PROCESSES AND EQUIPMENTS FOR PREPARING F<sub>2</sub>-CONTAINING  
GASES, AS WELL AS PROCESSES AND EQUIPMENTS  
FOR MODIFYING THE SURFACES OF ARTICLES

TECHNICAL FIELD

[0001] The present invention relates to processes and equipments for preparing F<sub>2</sub>-containing gases by exciting a fluoro compound under reduced pressure to generate an active species, and then raising the pressure to a normal pressure or overpressure condition to substantially wholly deactivate the generated active species, thereby generating fluorine (F<sub>2</sub>), as well as processes and equipments for modifying the surfaces of articles by contacting the F<sub>2</sub>-containing gas with the surfaces.

BACKGROUND ART

[0002] Plasma CVD is widely used to form thin films in the manufacture of semiconductor devices. In plasma CVD, a gaseous fluoro compound such as NF<sub>3</sub> is ionized, and the resulting ionized species are used for etching the surfaces of semiconductor substrates or cleaning CVD chambers. During such plasma ionization, F<sub>2</sub> gas is also generated, but F<sub>2</sub> gas is treated as exhaust gas.

[0003] For example, a method has been known for ionizing F<sub>2</sub> gas and using the resulting ionized species to clean the inner wall of a CVD chamber (e.g., see patent document 1), but this method uses a plasma of F<sub>2</sub> gas rather than F<sub>2</sub> gas itself.

[0004] Surface treatment methods for materials other

than semiconductors such as metal materials and plastic materials using a plasma derived from a fluoro compound have been reported (see patent document 2, and patent document 4). However, the plasma may penetrate into the article to be surface-treated to damage the article in these methods.

[0005] A surface treatment method using unionized  $F_2$  gas has also been reported (e.g., see patent document 3). However, the method directly using  $F_2$  gas has the following problems. First, it is difficult to store, transport and use a large amount of  $F_2$  gas because of the toxicity, hazardousness, reactivity, and corrosiveness of  $F_2$  gas. In order to reduce hazardousness, diluted  $F_2$  gas can be used, but costs for storage and transportation increase. Moreover, very stable materials must be used for the sites exposed to  $F_2$  gas, which add costs of the surface treatment equipment.

[0006] A method for treating the surface of an article comprising exciting a halogen compound by applying a low-frequency voltage on it at or near atmospheric pressure to decompose it and generate a halogen or hydrogen halide has also been proposed (see patent document 5). This method has the advantage that it is simple and safe to operate because it can be performed at or near atmospheric pressure. However, the concentration of the halogen or hydrogen halide that can be generated by this method is considerably low because of low decomposition efficiency and it is not easy to secure a sufficient concentration or amount for the

subsequent use.

References

Patent document 1: JP 2004-039740 A

Patent document 2: JP 2000-319433 A

Patent document 3: JP 2001-240956 A

Patent document 4: JP 08-217897 A

Patent document 5: JP 09-205272 A

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] The present invention was made under the circumstances as described above and provides processes for safely and easily preparing F<sub>2</sub> gas in simple equipments and such equipments. The present invention also provides processes and equipments enabling safe and easy surface modification by F<sub>2</sub> gas.

MEANS FOR SOLVEING THE PROBLEMS

[0008] As a result of careful studies to solve these problems, we accomplished the present invention on the basis of the finding that surface modification by F<sub>2</sub> gas can be safely and easily performed by supplying a gas containing a fluoro compound (a fluorine-containing compound) that is easier to handle than F<sub>2</sub> gas and converting the fluoro compound into F<sub>2</sub> gas before surface modification. We also accomplished the present invention on the basis of the finding that F<sub>2</sub> gas can be efficiently

generated in a sufficient concentration and amount from a fluoro compound by exciting the fluoro compound under reduced pressure to generate an active species and then raising the pressure to a normal pressure or overpressure condition to substantially wholly deactivate the active species generated.

[0009] Accordingly, the present invention provides the following.

[0010] (1) A process for preparing an F<sub>2</sub>-containing gas comprising the steps of:

exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas under reduced pressure; and

partially or completely converting the excited fluoro compound-containing gas containing the excited fluoro compound into F<sub>2</sub> under normal pressure or overpressure.

[0011] (2) The process for preparing an F<sub>2</sub>-containing gas as defined in (1) wherein the step of exciting a fluoro compound is performed in a first zone maintained under reduced pressure; and

the step of converting the gas into F<sub>2</sub> is performed in a second zone communicating with the first zone and maintained under normal pressure or overpressure.

[0012] (3) The process for preparing an F<sub>2</sub>-containing gas as defined in (1) wherein the step of exciting a fluoro compound is performed in a first zone maintained under reduced pressure; and

the step of converting the gas into F<sub>2</sub> comprises



maintaining the pressure in the transportation system under a normal pressure or overpressure condition during transportation of the excited fluoro compound-containing gas to a second zone communicating with the first zone.

[0013] (4) The process for preparing an  $F_2$ -containing gas as defined in (1) wherein the step of exciting a fluoro compound is performed in a first zone maintained under reduced pressure; and

the step of converting the gas into  $F_2$  is performed by maintaining the pressure in the first zone under a normal pressure or overpressure condition.

[0014] (5) The process for preparing an  $F_2$ -containing gas as defined in (1) wherein the step of exciting a fluoro compound is performed in a first chamber maintained under reduced pressure; and

the step of converting the gas into  $F_2$  comprises transporting the excited fluoro compound-containing gas containing the excited fluoro compound from the first chamber to a second chamber maintained under normal pressure or overpressure via a gas channel connecting the first chamber and the second chamber.

[0015] (6) The process for preparing an  $F_2$ -containing gas as defined in (1) wherein the step of exciting a fluoro compound is performed in a first chamber maintained under reduced pressure; and

the step of converting the gas into  $F_2$  comprises maintaining the pressure in the transportation system under a normal pressure or overpressure condition during

transportation of the excited fluoro compound-containing gas containing the excited fluoro compound from the first chamber to a second chamber via a gas channel connecting the first chamber and the second chamber.

[0016] (7) The process for preparing an  $F_2$ -containing gas as defined in (1) wherein the step of exciting a fluoro compound is performed in a first chamber maintained under reduced pressure; and

the step of converting the gas into  $F_2$  is performed in the first chamber by maintaining the first chamber under normal pressure or overpressure.

[0017] (8) The process for preparing an  $F_2$ -containing gas as defined in (5) or (6) wherein a vacuum pump is provided in a gas channel connecting the first chamber and the second chamber and said vacuum pump is used during the step of transporting the excited fluoro compound-containing gas from the first chamber to the second chamber.

[0018] (9) The process for preparing an  $F_2$ -containing gas as defined in any one of (1) to (8) wherein the step of exciting a fluoro compound comprises ionizing the fluoro compound-containing gas.

[0019] (10) The process for preparing an  $F_2$ -containing gas as defined in any one of (1) to (9) wherein the fluoro compound is a gaseous fluoro compound selected from linear, branched or cyclic saturated perfluorocarbons, linear, branched or cyclic unsaturated perfluorocarbons, carbonyl fluorides, perfluoro hypofluorides, perfluoro peroxides, perfluoroether compounds, oxygen-containing fluorides,

interhalogen fluorides, iodine-containing fluorides, sulfur-containing fluorides, nitrogen-containing fluorides, silicon-containing fluorides, rare gas-containing fluorides, or combinations thereof.

[0020] (11) The process for preparing an F<sub>2</sub>-containing gas as defined in any one of (1) to (9) wherein the fluoro compound is selected from CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>10</sub>, C<sub>5</sub>F<sub>12</sub>, C<sub>6</sub>F<sub>14</sub>, C<sub>2</sub>F<sub>4</sub>, C<sub>3</sub>F<sub>6</sub>, C<sub>4</sub>F<sub>8</sub>, C<sub>5</sub>F<sub>10</sub>, C<sub>6</sub>F<sub>12</sub>, C<sub>4</sub>F<sub>6</sub>, FCOF, CF<sub>3</sub>COF, CF<sub>2</sub>(COF)<sub>2</sub>, C<sub>3</sub>F<sub>7</sub>COF, CF<sub>3</sub>OF, C<sub>2</sub>F<sub>5</sub>OF, CF<sub>2</sub>(OF)<sub>2</sub>, CF<sub>3</sub>COOF, CF<sub>3</sub>OOCF<sub>3</sub>, CF<sub>3</sub>COOOF, CF<sub>3</sub>OCF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>OC<sub>2</sub>F<sub>5</sub>, C<sub>2</sub>F<sub>4</sub>OC<sub>2</sub>F<sub>4</sub>, OF<sub>2</sub>, SOF<sub>2</sub>, SOF<sub>4</sub>, NOF, ClF<sub>3</sub>, IF<sub>5</sub>, BrF<sub>5</sub>, BrF<sub>3</sub>, CF<sub>3</sub>I, C<sub>2</sub>F<sub>5</sub>I, N<sub>2</sub>F<sub>4</sub>, NF<sub>3</sub>, NOF<sub>3</sub>, SiF<sub>4</sub>, Si<sub>2</sub>F<sub>6</sub>, XeF<sub>2</sub>, XeF<sub>4</sub>, KrF<sub>2</sub>, SF<sub>4</sub>, SF<sub>6</sub>, or a mixture thereof.

[0021] (12) The process for preparing an F<sub>2</sub>-containing gas as defined in any one of (1) to (11) wherein the fluoro compound-containing gas comprises an inert gas and/or oxygen.

[0022] (13) The process for preparing an F<sub>2</sub>-containing gas as defined in (12) wherein the inert gas is He, Ne, Ar, Xe, Kr, N<sub>2</sub>, or a combination thereof.

[0023] (14) The process for preparing an F<sub>2</sub>-containing gas as defined in any one of (1) to (13) wherein the fluoro compound is one or more members selected from the group consisting of NF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, and COF<sub>2</sub>.

[0024] (15) The process for preparing an F<sub>2</sub>-containing gas as defined in (14) wherein the fluoro compound is ionized in the presence of oxygen when it is a perfluorocarbon or a mixture containing one or more perfluorocarbons.

[0025] (16) A process for modifying the surface of an article comprising contacting an F<sub>2</sub>-containing gas obtained by the process for preparing an F<sub>2</sub>-containing gas as defined in any one of (1) to (15) with the surface of the article under reduced pressure or overpressure or normal pressure.

[0026] (17) The surface modification process as defined in (16) further comprising the step of introducing an inert gas and/or oxygen after conferring energy on the fluoro compound-containing gas before contacting the gas with the article to be surface-modified.

[0027] (18) The surface modification process as defined in (16) or (17) wherein the surface modification is performed by fluorinating the surface of the article.

[0028] (19) The surface modification process as defined in any one of (16) to (18) wherein the article to be surface-modified is one or more members selected from the group consisting of metals, metal compounds and polymers.

[0029] (20) The surface modification process as defined in (19) wherein the polymer is an article based on polypropylene.

[0030] (21) The surface modification process as defined in (19) wherein the metal compound is one or more members selected from the group consisting of metal oxides, metal nitrides, metal carbides, metal hydroxides and metal chlorides.

[0031] (22) The surface modification process as defined in (19) wherein the metal compound is a compound based on

Si:

[0032] (23) The surface modification process as defined in (22) wherein the compound based on Si is Si, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiC, polysilicon, amorphous silicon, or a combination thereof.

[0033] (24) The surface modification process as defined in (22) wherein the compound based on Si is deposited in an LPCVD equipment.

[0034] (25) An equipment for preparing an F<sub>2</sub>-containing gas comprising:

a means for ionizing a fluoro compound-containing gas under reduced pressure; and

a pressure controlling means communicating with the ionizing means and controlling the pressure of the ionized fluoro compound-containing gas at a normal pressure or overpressure condition.

[0035] (26) A surface modification equipment comprising a means communicating with the pressure controlling means in the equipment for preparing an F<sub>2</sub>-containing gas as defined in (25) and positioning an article whose surface should be contacted with the F<sub>2</sub>-containing gas prepared in the equipment for preparing an F<sub>2</sub>-containing gas under reduced pressure or overpressure or normal pressure.

[0036] (27) The surface modification equipment as defined in (26) further comprising a vacuum pump or compressor communicating with the means for positioning the article.

[0037] (28) A method for using the equipment as defined



in any one of (25) to (27) to directly fluorinate an organic and/or inorganic material.

#### ADVANTAGES OF THE INVENTION

[0038] According to the present invention,  $F_2$  gas can be prepared from a fluoro compound and used in an amount necessary for each application, especially for surface modification of a material or synthetic reaction using  $F_2$  gas, thereby eliminating the necessity of providing/storing a large amount of hard-to-handle  $F_2$  gas in advance.

#### BRIEF EXPLANATION OF THE DRAWINGS

[0039] [Figure 1] Figure 1 shows an example of a surface modification equipment of the present invention.

#### THE MOST PREFERRED EMBODIMENTS OF THE INVENTION

[0040] In the present invention, the first zone for conferring energy on a fluoro compound-containing gas and the second zone for modifying the surface of an article may be provided in the same chamber. As used herein, the first zone refers to a space in which energy is conferred on a fluoro compound-containing gas by an energy conferring means, and the second zone refers to a space in which an article to be surface-modified is placed. The first zone and the second zone are in gaseous communication, and the fluoro compound-containing gas flows in gas phase from the first zone to the second zone. The first and second zones may be placed at different locations in the same chamber.

For example, when the energy conferring means and the means for mounting an article to be surface-modified are placed at different locations, the space containing the former is the first zone and the space containing the latter is the second zone.

[0041] The first zone and the second zone may be different chambers. In this case, the first zone and the second zone form a first chamber and a second chamber, respectively. The first chamber and the second chamber are brought into gaseous communication by any known method. For example, the first chamber and the second chamber are connected via a gas channel so that the fluoro compound-containing gas flows from the first zone to the second zone via the gas channel.

[0042] A partition wall may be provided between the first zone and the second zone while keeping communication therebetween. In this case, the pressure in the first and second zones can be independently varied by operatively evacuating the first zone and/or second zone. When the first zone is under reduced pressure and the second zone is at a pressure higher than that of the first zone, the excited fluoro compound can be partially or completely converted into  $F_2$  by raising the pressure. However, conversion into  $F_2$  is not limited to such an embodiment, but may also be performed in the first zone or during transportation from the first zone to the second zone.

[0043] In the present invention, the fluoro compound in the fluoro compound-containing gas supplied to the first

zone is not specifically limited, but any compound can be used so far as it is excited by conferring energy and decomposed and then produces  $F_2$  gas and it is easier to handle than  $F_2$  gas. In terms of ease of handling, fluoro compounds that are gaseous in use conditions are preferred. For example, compounds that are gaseous at  $25^\circ C$ , 1 atm are preferred.

[0044] Fluoro compounds include linear, branched or cyclic saturated perfluorocarbons; linear, branched or cyclic unsaturated perfluorocarbons, carbonyl fluorides, perfluoro hypofluorides, perfluoro peroxides, perfluoroether compounds, oxygen-containing fluorides, interhalogen fluorides, iodine-containing fluorides, sulfur-containing fluorides, nitrogen-containing fluorides, silicon-containing fluorides, rare gas-containing fluorides, or combinations thereof.

[0045] As used herein, the perfluorocarbon refers to a hydrocarbon in which all the H atoms have been replaced by F atoms. As used herein, substituted or unsubstituted hydrocarbon groups without prefix or without distinction between structural isomers include all isomers unless otherwise indicated. For example,  $C_4F_{10}$  includes n- $C_4F_{10}$  and i- $C_4F_{10}$ . The cyclic compounds may be monocyclic compounds or polycyclic compounds, alicyclic compounds or aromatic compounds, or carbocyclic compounds or heterocyclic compounds.

[0046] The saturated perfluorocarbon refers to a perfluorocarbon having no carbon-carbon multiple bonds.

The number of carbon atoms in the saturated perfluorocarbon is not specifically limited, but preferably 1-8, more preferably 1-6. Linear saturated perfluorocarbons include  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $n\text{-C}_4\text{F}_{10}$ ,  $n\text{-C}_5\text{F}_{12}$ , and  $n\text{-C}_6\text{F}_{14}$ ; branched saturated perfluorocarbons include  $i\text{-C}_4\text{F}_{10}$ ,  $i\text{-C}_5\text{F}_{12}$ ,  $\text{C}(\text{CF}_3)_4$ ,  $i\text{-C}_6\text{F}_{14}$ ,  $\text{C}_3\text{F}_7\text{CF}(\text{CF}_3)_2$ ; and cyclic perfluorocarbons include  $\text{C}_6\text{F}_{12}$ .

[0047] The unsaturated perfluorocarbon refers to a perfluorocarbon having at least one carbon-carbon double bond and/or triple bond. The number of carbon atoms in the unsaturated perfluorocarbon is not specifically limited, but preferably 2-8, more preferably 2-6. For example, unsaturated perfluorocarbons include  $\text{C}_2\text{F}_4$ ,  $\text{C}_3\text{F}_6$ ,  $\text{CF}(\text{CF}_3)=\text{CF}(\text{CF}_3)$ ,  $\text{CF}_2=\text{C}(\text{C}_2\text{F}_5)\text{F}$ ,  $\text{CF}_2=\text{C}(\text{CF}_3)_2$ ,  $c\text{-C}_4\text{F}_8$ ,  $\text{CF}\equiv\text{CC}_2\text{F}_5$ ,  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ ,  $\text{C}_5\text{F}_{10}$ ,  $\text{C}_6\text{F}_{12}$ ,  $\text{C}_2\text{F}_2$ ,  $\text{C}_3\text{F}_4$ ,  $\text{C}_4\text{F}_6$ .

[0048] The carbonyl fluoride refers to a compound containing a carbonyl group and fluorine. Carbonyl fluorides include  $\text{FCOF}$ ,  $\text{CF}_3\text{COF}$ ,  $\text{CF}_2(\text{COF})_2$ , and  $\text{C}_3\text{F}_7\text{COF}$ .

[0049] The perfluoro peroxide refers to a peroxide in which all the H atoms have been replaced by F atoms, such as  $\text{CF}_3\text{OOCF}_3$ .

[0050] The perfluoroether compound refers to an ether in which all the H atoms have been replaced by F atoms, such as  $\text{CF}_3\text{OCF}_3$ ,  $\text{C}_2\text{F}_5\text{OC}_2\text{F}_5$ , and  $\text{C}_2\text{F}_4\text{OC}_2\text{F}_4$ .

[0051] The perfluoro hypofluoride refers to a compound having a structure obtained by replacing all the -OH groups of a compound having at least one -OH group by -OF groups and replacing all the H atoms other than -OH groups by F

atoms. Perfluoro hypofluorides include  $\text{CF}_3\text{OF}$ ,  $\text{C}_2\text{F}_5\text{OF}$ ,  $\text{CF}_2(\text{OF})_2$ , and  $\text{CF}_3\text{COOF}$ .

[0052] Oxygen-containing fluorides include  $\text{OF}_2$ ,  $\text{SOF}_2$ ,  $\text{SOF}_4$ ,  $\text{NOF}$  and  $\text{NOF}_3$  in addition to the carbonyl fluorides, perfluoro peroxides and perfluoroether compounds described above.

[0053] The interhalogen fluoride refers to a compound in which a bond has been formed between a halogen other than fluorine and fluorine. Interhalogen fluorides include  $\text{ClF}_3$ ,  $\text{IF}_5$ ,  $\text{BrF}_5$ , and  $\text{BrF}_3$ .

[0054] The iodine-containing fluoride refers to a compound containing iodine and fluorine, such as  $\text{CF}_3\text{I}$ , and  $\text{C}_2\text{F}_5\text{I}$ .

[0055] The nitrogen-containing fluoride refers to a compound containing nitrogen and fluorine, such as  $\text{N}_2\text{F}_4$ ,  $\text{NF}_3$ ,  $\text{NOF}$ ,  $\text{NOF}_3$ .

[0056] The silicon-containing fluoride refers to a compound containing silicon and fluorine, such as  $\text{SiF}_4$ ,  $\text{Si}_2\text{F}_6$ .

The rare gas-containing fluoride refers to a compound containing a rare gas and fluorine, such as  $\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{KrF}_2$ .

[0057] The sulfur-containing fluoride refers to a compound containing sulfur and fluorine, such as  $\text{SF}_4$ ,  $\text{SF}_6$ ,  $\text{SOF}_2$ , and  $\text{SOF}_4$ .

[0058] These fluoro compounds may be used alone or in combination.

[0059] The fluoro compound-containing gas supplied to



the first zone may contain a gas other than the fluoro compound. The type and flow rate of the gas other than the fluoro compound and the pressure in the first zone is selected depending on the mode of exciting the fluoro compound in the first zone and the intended concentration of  $F_2$  generated. When a plasma is generated in the first zone, an inert gas and/or oxygen can be used as the gas other than the fluoro compound. Inert gases include He, Ne, Ar, Xe, Kr,  $N_2$ , or a combination thereof. When the fluoro compound is a nitrogen-containing fluoro compound, Ar is preferred, and when the fluoro compound is a perfluorocarbon,  $O_2$  is preferred.

[0060] Methods for exciting the fluoro compound by conferring energy in the first zone are not specifically limited so far as  $F_2$  is generated after excitation, e.g., plasma ionization, irradiation, and heating. Excitation refers to transition to an energy state higher than the ground state. For plasma ionization, any known method can be used, such as inductively coupled plasma (ICP), helicon wave plasma, and electron cyclotron resonance plasma (ECR). Irradiations include UV irradiation and laser irradiation. If the fluoro compound is thermally decomposed to generate  $F_2$ , heating can be used as energy conferring means.

[0061] The gas containing the fluoro compound excited in the first zone generates  $F_2$  before it is contacted with an article to be surface-modified in the second zone.  $F_2$  can be generated at any site and any time, i.e., it can be generated in the first zone, or during transportation from

the first zone to the second zone, or in the second zone. When the first zone and second zone are different chambers,  $F_2$  can be generated in a gas channel connecting both.  $F_2$  can be generated by any reaction mechanism, including recombination of the F radicals generated by excitation, for example.

[0062] When the fluoro compound-containing gas contains two or more fluoro compounds,  $F_2$  can be generated from all species of fluoro compounds or a part of species of fluoro compounds can contribute to  $F_2$  generation. The proportion of fluoro compounds converted into  $F_2$  is preferably higher, and the total amounts of fluoro compounds may be converted into  $F_2$ . The gas containing the fluoro compound when it is supplied to the first zone is herein referred to as "fluoro compound-containing gas". The gas containing the fluoro compound excited in the first zone is referred to as "excited fluoro compound-containing gas". The "excited fluoro compound-containing gas" may sometimes contain  $F_2$  derived from the excited fluoro compound.

[0063] The fluoro compound-containing gas treated in the first zone is transported to the second zone. The fluoro compound-containing gas treated in the first zone may generate  $F_2$  gas in the first zone or may generate  $F_2$  gas as time goes by. The generation of  $F_2$  gas can be promoted by increasing the total pressure of the fluoro compound-containing gas and/or the partial pressure of the excited fluoro compound. Thus, when the first chamber and the second chamber communicate via a gas channel, the fluoro

compound-containing gas can be transported to the second chamber without removing it outside.

[0064] Processes of the present invention offer the advantage that there is no necessity of providing or transporting or otherwise handling a large amount of  $F_2$  gas in advance because  $F_2$  gas in an amount necessary for surface modification is prepared in a first zone by exciting a fluoro compound and consumed in a second zone. In other words, the conventional problems with handling of  $F_2$  gas can be solved by storing  $F_2$  gas in the form of a fluoro compound that is safer and easier to handle than  $F_2$  gas before surface modification and converting the fluoro compound into  $F_2$  gas to use it for surface modification.

[0065] After the fluoro compound is excited and before it is contacted with an article to be surface-modified, the fluoro compound may be mixed with another gas. The additional gas to be mixed is preferably an inert gas. The inert gas here has the meaning as defined above. The additional gas can be introduced anywhere in the first zone and second zone. When the first zone and the second zone are different chambers, the additional gas can be introduced anywhere in the first chamber, in the second chamber, and in the gas channel connecting the first chamber and the second chamber.

[0066] At the point when the excited fluoro compound-containing gas is removed from the first zone, it may contain  $F_2$ . In view of the hazardousness and reactivity of  $F_2$  gas, the  $F_2$  gas concentration of the  $F_2$ -containing gas is

preferably low.

[0067] To remove the fluoro compound-containing gas from the first chamber, the first chamber may be evacuated via a vacuum pump and the discharged fluoro compound-containing gas may be introduced into the second chamber. The vacuum pump can be provided in a gas channel connecting the first chamber and the second chamber. When a vacuum pump is used, the fluoro compound may be mixed with another gas between the first chamber and the vacuum pump or between the vacuum pump and the second chamber.

[0068] The flow rate of the additional gas to be mixed after removal from the first zone and the pressure in the second zone are selected depending on the material and surface area of the article to be surface-modified.

[0069] The article to be surface-modified is not specifically limited and may be made from any material so far as it reacts with  $F_2$  gas upon contact with it. Preferably, the surface is fluorinated by contacting the surface with  $F_2$  gas. Various properties such as water repellency, oil repellency, soil resistance and weather resistance can be improved by surface fluorination. In view of the reaction with  $F_2$  gas, the article to be surface-modified preferably comprises a metal and/or metal compound and/or polymer, more preferably comprises a metal and/or metal compound and/or polymer on the surface.

[0070] Metals include, for example, elemental metals such as iron, aluminum, titanium, zinc, nickel, tin and copper; and alloys such as stainless steel and brass.

Metal compounds include one or more members selected from the group consisting of metal oxides, metal nitrides, metal carbides, metal hydroxides and metal chlorides, e.g., a compound based on Si, i.e., Si, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiC, polysilicon, amorphous silicon, or a combination thereof. The compound based on Si may be deposited in an LPCVD equipment. Polymers include polyethylenes such as HDPE, LDPE, LLDPE; polypropylene; polyesters such as polyethylene terephthalate and polyethylene naphthalate; polyvinyl chloride, polyvinylidene chloride, nylon, polyvinyl acetate, polyvinyl alcohol, polyvinyl acetal, polystyrene, etc.

[0071] The present invention also relates to a surface modification equipment comprising a first zone and a second zone, as well as a surface modification equipment comprising a first chamber, a second chamber, and a gas channel connecting the first chamber and the second chamber.

[0072] The first zone includes an energy conferring means, which confers energy on a fluoro compound-containing gas, thereby exciting at least one fluoro compound in the fluoro compound-containing gas. The energy conferring means include plasma generators, light sources, and heat sources. Plasma generators include ECR plasma generators, ICP plasma generators, and helical plasma generators. Light sources include xenon lamps, excimer lasers, etc. Heat sources include electric furnaces.

[0073] After the fluoro compound is excited in the first zone, the excited fluoro compound-containing gas is transported to the second zone. When the first and second



zone are different chambers, the excited fluoro compound-containing gas flows via a gas channel connecting the first chamber and second chamber. The surface modification equipment of the present invention may further comprise a vacuum pump in the gas channel.

[0074] The surface modification equipment of the present invention may further comprise a means for mixing the excited fluoro compound-containing gas and an inert gas. The means for mixing the excited fluoro compound-containing gas and an inert gas is not specifically limited, and the equipment may be simply designed so that the excited fluoro compound-containing gas channel and the inert gas channel join.

[0075] The second zone can include a means for introducing an article to be surface-modified. The introducing means is not specifically limited, and a movable stage may be introduced via a sample introducing chamber. The gas discharged from the second zone is sent to an exhaust gas treatment facility because  $F_2$  or a fluoro compound may remain in it.

[0076] An embodiment of the present invention for exciting a fluoro compound-containing gas by plasma ionization is explained below with reference to Figure 1.

[0077] In the surface modification equipment of Figure 1, the first chamber includes a plasma generator, which is evacuated to a pressure suitable for plasma generation, preferably 1-1333 Pa. After evacuation, a fluoro compound capable of generating  $F_2$  gas by plasma ionization such as

an NF<sub>3</sub>-containing gas is supplied to the first chamber. The fluoro compound may be mixed with another gas such as N<sub>2</sub> or Ar before it is supplied to the first chamber. In this case, a gas containing the fluoro compound and the additional gas is supplied to the first chamber as a fluoro compound-containing gas. In other words, the supplied fluoro compound-containing gas may be NF<sub>3</sub> alone or a mixed gas of NF<sub>3</sub> and N<sub>2</sub>.

[0078] If NF<sub>3</sub> is completely converted into F<sub>2</sub> as shown below:



when the fluoro compound-containing gas is NF<sub>3</sub> alone, 25% nitrogen gas is generated and therefore, the concentration of the F<sub>2</sub> gas generated is 75% at maximum. One of preferred features of the present invention is that substantially complete decomposition of NF<sub>3</sub> can be achieved.

[0079] As the amount of NF<sub>3</sub> that can be introduced is 100 sccm - 5000 sccm, the amount of F<sub>2</sub> gas generated is 150 sccm - 7500 sccm. An inert gas is introduced upstream of the treating chamber if one wishes to use the F<sub>2</sub> gas at a more dilute concentration than 75%, or it is introduced upstream of the vacuum pump if one wishes to handle the F<sub>2</sub> gas at a concentration as low as possible. Alternatively, an inert gas is introduced upstream of the plasma generator and controlled to a desired concentration provided that the conditions for generating a plasma are satisfied. This dilute fluorine gas is introduced into the treating chamber downstream in the line, in which it is used for surface

modification of an article under reduced pressure or normal pressure or overpressure.

[0080] The working conditions of the plasma generator in the first chamber are selected to excite the fluoro compound supplied. The working conditions are selected to increase the decomposition rate of the fluoro compound, preferably to completely decompose the fluoro compound.

[0081] The excited fluoro compound-containing gas is transported from the first chamber to the second chamber via the gas channel. In the gas channel, the excited fluoro compound-containing gas is mixed with another gas to control the  $F_2$  concentration to a level suitable for surface modification. The additional gas can be added from any one or more of the three inlets shown in the figure. Alternatively, no additional gas may be added and a fluoro compound-containing gas containing a fluoro compound mixed with another gas may be provided in advance.

[0082] In the second chamber, surface modification takes place. The gas discharged from the second chamber is introduced into an exhaust gas treatment facility.

[0083] In the equipment of Figure 1, the pressure is maintained at a level lower than atmospheric pressure (or normal pressure) upstream of the vacuum pump, then at atmospheric pressure downstream of the vacuum pump and upstream of the surface treating chamber, and then at reduced pressure or overpressure or atmospheric pressure in the surface treating chamber. However, the present invention is not limited to the embodiment of Figure 1, but

the pressure downstream of the vacuum pump may be raised by adding another gas. Preferred pressure conditions include 1-1333 Pa upstream of the vacuum pump and atmospheric pressure or more downstream of the vacuum pump.

#### INDUSTRIAL APPLICABILITY

[0084] According to the present invention, a large amount of hard-to-handle  $F_2$  can be easily prepared in any concentration range when needed. Therefore, it is very useful for all industries using  $F_2$ . Especially, the present invention is useful for industries taking advantage of the reactivity of  $F_2$  such as semiconductor manufacturing industry and pharmaceutical and agricultural chemical manufacturing industry as well as industries taking advantage of fluorinated materials prepared by reactions with  $F_2$  such as polymer material manufacturing industry, inorganic material manufacturing industry, metal material manufacturing industry, organic material manufacturing industry and battery material manufacturing industry.

#### EXAMPLES

[0085] The following examples illustrate the present invention without, however, limiting the present invention thereto.

##### [Example 1]

$F_2$  was prepared from a fluoro compound-containing gas using the equipment of Figure 1.  $NF_3$  was used as the fluoro

compound gas, and an inductively coupled plasma (ICP) generator (Litmas Blue 1200 from Landmark Technology) was used as the plasma generator.

[0086] First, the first chamber including the plasma generator was evacuated to 1 Torr (133 Pa). Then,  $\text{NF}_3$  (flow rate: 200 sccm) was diluted with Ar (flow rate: 300 sccm) at diluting gas inlet 1 to prepare a fluoro compound-containing gas, and the fluoro compound-containing gas was supplied to the first chamber. A power of 1200 W was applied to the plasma generator. The fluoro compound-containing gas discharged from the first chamber was diluted again with nitrogen (flow rate: 9300 sccm) at diluting gas inlet 3 and transported to the treating chamber (second chamber) maintained under normal pressure downstream of the vacuum pump.

[0087] Theoretically, if  $\text{NF}_3$  supplied at the  $\text{NF}_3$  flow rate of the present example is completely decomposed ( $\text{NF}_3 \rightarrow 1/2\text{N}_2 + 3/2\text{F}_2$ ),  $\text{N}_2$  and  $\text{F}_2$  will be generated at 100 sccm and 300 sccm, respectively. Thus, if  $\text{NF}_3$  is completely decomposed, the  $\text{F}_2$  concentration after dilution with nitrogen will be 3.0 vol %.

[0088] The fluoro compound-containing gas was sampled between the vacuum pump and the second chamber and analyzed by FT-IR and titrated with a 10% KI aqueous solution. The FT-IR analyzer used was FT-IR IGA-2000 from Midac. As a result, the concentration of  $\text{F}_2$  in the fluoro compound-containing gas was 2.9 vol %, showing that the decomposition rate of  $\text{NF}_3$  supplied to the first chamber was

98%.

[0089] Then, surface treatment of polypropylene plates was performed in the second chamber. The second chamber used was a cylindrical vessel made from Ni having an inner volume of 4.6 L. Five polypropylene plates (hereinafter sometimes abbreviated as PP; L x W x H = 20 mm x 20 mm x 2 mm) were placed in this vessel and the atmosphere in the second chamber was replaced by nitrogen gas. Then, the fluoro compound-containing gas obtained by the operation above was transported into the second chamber and surface treatment of PP was performed at 25°C for a predetermined period. The contact angles on PP surfaces (contact angles of water expressed in degrees) were measured at various treating times (the contact angle on PP before treatment: 89 degrees). The measurement results are shown in Table 1 (the calculated average of five PPs (n=5)).

[Example 2]

An experiment similar to Example 1 was performed except that the flow rate of nitrogen for diluting the fluoro compound-containing gas discharged from the first chamber including the plasma generator was changed to 5300 sccm. If  $\text{NF}_3$  is completely decomposed under these conditions, the concentration of  $\text{F}_2$  in the fluoro compound-containing gas transported to the second chamber maintained under normal pressure downstream of the vacuum pump will be 5.0 vol %.

[0090] The concentration of  $\text{F}_2$  in a sampled fluoro



compound-containing gas was 4.9 vol %, showing that the decomposition rate of  $\text{NF}_3$  was 98%.

[0091] Then, surface treatment of PP was performed in the same manner as in Example 1 and the contact angles were measured. The measurement results are shown in Table 1.

[0092] [Table 1]

Table 1: Contact angles on surfaces (in degrees)

Treating time	1 min	5 min	10 min	30 min	60 min
Example					
1	89	89	101	104	105
2	94	102	103	105	105

[0093] [Example 3]

An experiment similar to Example 1 was performed except that  $\text{C}_2\text{F}_6$  was used in place of  $\text{NF}_3$  as the fluoro compound, a fluoro compound-containing gas was generated by diluting  $\text{C}_2\text{F}_6$  (flow rate: 40 sccm) with  $\text{O}_2$  (flow rate: 160 sccm) and supplied to the first chamber including the plasma generator and the fluoro compound-containing gas discharged from the first chamber was diluted with nitrogen at a flow rate of 100 slm.

[0094] In a sampled fluoro compound-containing gas, 710 ppm  $\text{F}_2$  gas was detected, and the decomposition rate of  $\text{C}_2\text{F}_6$  supplied was approximately 100%.

[0095] Then, surface treatment was performed in the same manner as in Example 1 except that the fluoro compound-containing gas diluted with nitrogen as described above was used and aluminum plates were used in place of the

polypropylene plates. Five aluminum plates (hereinafter sometimes abbreviated as Al; L x W x H = 20 mm x 20 mm x 2 mm) were placed in a cylindrical vessel made from Ni having an inner volume of 4.6 L (second chamber) and the atmosphere in the second chamber was replaced by nitrogen gas. Then, the fluoro compound-containing gas obtained by the operation above was transported into the second chamber and surface treatment of Al was performed at 25°C for a predetermined period, and the contact angles on Al surfaces (contact angles of water expressed in degrees) were measured at various treating times.

[0096] The measurement results are shown in Table 2.

[Example 4]

An experiment similar to Example 3 was performed except that FCOF was used in place of  $C_2F_6$  as the fluoro compound.

[0097] In a sampled fluoro compound-containing gas, 140 ppm  $F_2$  gas was detected, and the decomposition rate of FCOF supplied was 69%.

[0098] Then, surface treatment of copper plates (sometimes abbreviated as Cu) in place of Al was performed and the contact angles were measured in the same manner as in Example 3. In this case, Cu was preliminarily acid-washed (Cu was stirred in a 0.1N HCl solution for 30 min and then washed with water three times) and heated (heated in the atmosphere at 200°C for 1 hr and then allowed to cool in a desiccator). The measurement results are shown

in Table 2.

[0099] [Table 2]

Table 2: Contact angles on surfaces (in degrees)

Treating time Example	10 min	30 min	60 min	120 min	180 min
3	93	105	109	108	109
4	94	102	109	109	108

[0100] [Example 5]

Using the equipment of Figure 1, surface modification of polypropylene was performed.  $\text{NF}_3$  was used as the fluoro compound gas, and an inductively coupled plasma (ICP) generator (Litmas Blue 1200 from Landmark Technology) was used as the plasma generator. A polypropylene (PP) sample of  $L \times W \times H = 20 \text{ mm} \times 20 \text{ mm} \times 2 \text{ mm}$  was placed in the second chamber.

[0101] First, the first chamber was evacuated to 1 Torr. Then,  $\text{NF}_3$  (flow rate: 100 sccm) was diluted with Ar (flow rate: 400 sccm) at inlet 1 to prepare a fluoro compound-containing gas, and the fluoro compound-containing gas was supplied to the first chamber. A power of 1200 W was applied to the plasma generator. The fluoro compound-containing gas discharged from the first chamber was diluted again with nitrogen (flow rate: 14400 sccm) at inlet 3 and introduced into the second chamber maintained under normal pressure. If  $\text{NF}_3$  is completely decomposed under these conditions, the concentration of  $\text{F}_2$  in the

fluoro compound-containing gas introduced into the second chamber will be 1 vol % (the results of sample analyses showed that the F<sub>2</sub> concentration was 0.99 vol % and the decomposition rate was 99%).

[0102] In the second chamber, the PP sample was contacted with the fluoro compound-containing gas under normal pressure at 24°C for 3 hrs.

[0103] The sample surface was analyzed by XPS PHI Quantum 2000 from ULVAC-PHI. Before treatment, the atomic concentration of carbon on the sample surface was 83 atom % and the atomic concentration of fluorine was 0 atom %, but after treatment, the atomic concentration of carbon was 49 atom % and the atomic concentration of fluorine was 44 atom %. The results of this analysis by XPS show that the sample surface has been fluorinated.

[0104] Conditions of analysis by XPS are as follows.

[0105] X-ray source: Al Ka 1486.6 eV monochromatic

X-ray output: 24.72 W

X-ray beam diameter: 100.0 mm

Source to analyzer angle: 45.0°

Neutralizer energy: 1.0 V

Neutralizer current: 25.0 nA

In-depth analyses

Sputter ion: Ar<sup>+</sup>

Sputter energy: 3.000 keV

Sputter current: 25.0 nA.

[Example 6]

Surface modification of a PP sample was performed in the same manner as in Example 5 except that  $\text{NF}_3$  (flow rate: 200 sccm) was diluted with Ar (flow rate: 300 sccm) to prepare a fluoro compound-containing gas and the fluoro compound-containing gas discharged from the first chamber was diluted with nitrogen at a flow rate of 9300 sccm. If  $\text{NF}_3$  is completely decomposed, the concentration of  $\text{F}_2$  in the fluoro compound-containing gas introduced into the second chamber will be 3 vol % (the results of sample analyses showed that the  $\text{F}_2$  concentration was 2.9 vol % and the decomposition rate was 99%).

[0106] After surface treatment, the surface of the PP sample was analyzed by XPS PHI Quantum 2000 from ULVAC-PHI in the same manner as in Example 5. Before treatment, the atomic concentration of carbon on the sample surface was 83 atom % and the atomic concentration of fluorine was 0 atom %, but after treatment, the atomic concentration of carbon was 41 atom % and the atomic concentration of fluorine was 53 atom %. These results show that the sample surface has been fluorinated.

[Example 7]

Using the equipment of Figure 1, an etching test was performed on a wafer with  $\text{SiO}_2$  film. A wafer (25 mm x 25 mm) having an  $\text{SiO}_2$  film (7500 angstroms) on single-crystal Si was placed in a cylindrical vessel made from Ni having an inner volume of 4.6 L (second chamber). Upstream of this second chamber, an inductively coupled plasma (ICP)

generator (ASTRONi from ASTeX) was provided as the plasma generator (first chamber). The atmosphere in the first and second chambers was replaced by nitrogen. Then, the second chamber was evacuated to  $0.5 \times 10^5$  Pa, and heated to predetermined temperatures (260°C and 310°C).  $\text{NF}_3$  (1000 sccm) was supplied into the first chamber and decomposed, and the fluoro compound-containing gas discharged from the first chamber was diluted with nitrogen (flow rate: 5500 sccm) at diluting gas inlet 3. The pressure near diluting gas inlet 3 was normal pressure. Thus, a fluoro compound-containing gas containing  $\text{F}_2$  at a concentration of 20 vol % was generated. Of this fluoro compound-containing gas, 1000 sccm was transported into the second chamber maintained at  $0.5 \times 10^5$  Pa and each predetermined temperature, and the target wafer was surface treated at each temperature.

[0107] After treatment, the wafer was measured for film thickness using Nano Spec 3000AF-T from Nanometrics to determine the etching rate at each predetermined temperature. The results are shown in Table 3.

[0108] [Table 3]

Table 3: Etching rate of  $\text{SiO}_2$  film (in angstroms/min)

Treating temperature	Etching rate
260°C	60
310°C	280

[0109] [Example 8]

Using the surface treatment equipment of Figure 1,



compounds were fluorinated.

[0110] In the surface treatment equipment of Figure 1, a 1000 ml PFA reactor including a temperature-controlled bath was placed at the position of the treating chamber. In the reactor, 517 g (5.87 mol) of 1,3-dioxolan-2-one was introduced and molten in the temperature-controlled bath at 50°C. Then, dissolved gas components such as air were expelled from the system with a nitrogen gas stream at a flow rate of 200 sccm fed into the reactor for 30 min so that the atmosphere in the system was replaced by nitrogen. Then, F<sub>2</sub> was generated from NF<sub>3</sub> using NF<sub>3</sub> as the fluoro compound-containing gas and an inductively coupled plasma (ICP) generator (ASTRON1 from ASTeX) as the plasma generator. NF<sub>3</sub> (1000 sccm) was introduced and diluted with N<sub>2</sub> (3000 sccm) to give approximately 30% of F<sub>2</sub>. The pressure near diluting N<sub>2</sub> gas inlet 3 was normal pressure. Of the 30% F<sub>2</sub>, 350 sccm was introduced into the reactor using a gas nozzle fitted with an SUS filter (pore diameter 15 µm, surface area 7.5cm<sup>2</sup>). The reaction solution was constantly stirred by a stirrer at about 800 rpm to prevent fluorine gas from locally staying. The liquid phase temperature in the reactor was maintained at 50-60°C by an outer temperature-controlled bath. Simultaneously, the gas phase temperature was maintained at 35-50°C by condensing/refluxing the vapor of the starting material, product and by-produced hydrogen fluoride with a condenser provided at the top of the reactor. Uncondensed gases such as unreacted fluorine was treated in a scrubber provided

downstream of the condenser.

[0111] When the amount of fluorine introduced reached 10.6 mol (1.8 mol equivalents of the starting material), the reaction was terminated and the by-produced hydrogen fluoride was distilled off, and then the residue was washed with water (200 ml) and a 10 %  $\text{NaHCO}_3$  aqueous solution (100 ml), extracted with dichloromethane (6 x 500 ml). The extract was dried over anhydrous magnesium sulfate, and then dichloromethane was distilled off. The resulting crude product (590 g) was purified by distillation to give 480 g of 4-fluoro-1,3-dioxolan-2-one at a purity of 90% or more (yield about 70%).

[0112] The crude product at a purity of 90% was recrystallized at 15°C three times to give about 390 g of 4-fluoro-1,3-dioxolan-2-one at a purity of 99% or more.

[Comparative example 1]

In the equipment of Figure 1, a decomposition experiment of a fluoro compound ( $\text{NF}_3$ ) was performed to prepare a fluoro compound-containing gas in the same manner as in Example 1 except that the first chamber of the plasma generator and the second chamber of the treating chamber were connected without using the vacuum pump unlike Example 1 and the pressure in the treating chamber was maintained at 1.0 Torr similarly to the pressure in the plasma generator rather than normal pressure.

[0113] In this case, the concentration of  $\text{F}_2$  in a sampled fluoro compound-containing gas was 114 ppm.

[Comparative example 2]

In the equipment of Figure 1, a decomposition experiment of a fluoro compound ( $\text{NF}_3$ ) was performed to prepare a fluoro compound-containing gas in the same manner as in Example 1 except that the plasma generator and the treating chamber were connected without using the vacuum pump unlike Example 1 and the fluoro compound ( $\text{NF}_3$ ) was ionized at 1.0 Torr and the pressure in the treating chamber was adjusted to 0.48 Torr rather than normal pressure.

[0114] In this case, the concentration of  $\text{F}_2$  in a sampled fluoro compound-containing gas was 84 ppm.

[0115] In addition to the embodiments explained above, the present invention includes the following embodiments.

[A] A surface modification process comprising the steps of:

(1) exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas in a first zone maintained under reduced pressure;

(2) transporting the excited fluoro compound-containing gas containing the excited fluoro compound to a second zone communicating with the first zone and maintained under normal pressure or overpressure; and

(3) contacting an  $\text{F}_2$ -containing gas containing  $\text{F}_2$  gas generated by partial or complete conversion of the excited fluoro compound with the surface of an article in the second zone to modify the surface of the article;

(4) wherein the converted  $F_2$  gas is used before the fluoro compound excited in the first zone is partially or wholly contacted with the surface of the article in the second zone.

[0116] [B] A surface modification process comprising the steps of:

(1) exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas under a reduced pressure condition in a first zone;

(2) maintaining the pressure in the transportation system under a normal pressure or overpressure condition during transportation of the excited fluoro compound-containing gas containing the excited fluoro compound to a second zone communicating with the first zone; and

(3) contacting an  $F_2$ -containing gas containing  $F_2$  gas generated by partial or complete conversion of the excited fluoro compound with the surface of an article in the second zone to modify the surface of the article;

(4) wherein the converted  $F_2$  gas is used before the fluoro compound excited in the first zone is partially or wholly contacted with the surface of the article in the second zone.

[0117] [C] A surface modification process comprising the steps of:

(1) exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas under a reduced pressure condition

in a first zone;

(2) partially or completely converting the excited fluoro compound into an  $F_2$ -containing gas containing  $F_2$  by maintaining the pressure in the first zone under a normal pressure or overpressure condition;

(3) transporting the converted  $F_2$ -containing gas to a second zone communicating with the first zone; and

(4) contacting the  $F_2$ -containing gas containing  $F_2$  gas generated by partial or complete conversion of the excited fluoro compound with the surface of an article in the second zone to modify the surface of the article;

(5) wherein the converted  $F_2$  gas is used before the fluoro compound excited in the first zone is partially or wholly contacted with the surface of the article in the second zone.

[0118] [D] A surface modification process comprising the steps of:

(1) exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas in a first chamber maintained under reduced pressure;

(2) transporting the excited fluoro compound-containing gas containing the excited fluoro compound from the first chamber to a second chamber maintained under normal pressure or overpressure via a gas channel connecting the first chamber and the second chamber; and

(3) contacting an  $F_2$ -containing gas containing  $F_2$  gas generated by partial or complete conversion of the excited

fluoro compound with the surface of an article in the second chamber to modify the surface of the article;

(4) wherein the converted  $F_2$  gas is used before the fluoro compound excited in the first chamber is partially or wholly contacted with the surface of the article in the second chamber.

[0119] [E] A surface modification process comprising the steps of:

(1) exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas under a reduced pressure condition in a first chamber;

(2) maintaining the pressure in the transportation system under a normal pressure or overpressure condition during transportation of the excited fluoro compound-containing gas containing the excited fluoro compound from the first chamber to a second chamber via a gas channel connecting the first chamber and the second chamber; and

(3) contacting an  $F_2$ -containing gas containing  $F_2$  gas generated by partial or complete conversion of the excited fluoro compound with the surface of an article in the second chamber to modify the surface of the article;

(4) wherein the converted  $F_2$  gas is used before the fluoro compound excited in the first chamber is partially or wholly contacted with the surface of the article in the second chamber.

[0120] [F] A surface modification process comprising the steps of:



(1) exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas under a reduced pressure condition in a first chamber;

(2) partially or completely converting the excited fluoro compound into an  $F_2$ -containing gas containing  $F_2$  gas generated by such conversion by maintaining the pressure in the first chamber under a normal pressure or overpressure condition;

(3) transporting the converted  $F_2$ -containing gas from the first chamber to a second chamber via a gas channel connecting the first chamber and the second chamber; and

(4) contacting the  $F_2$ -containing gas containing  $F_2$  gas generated by partial or complete conversion of the excited fluoro compound with the surface of an article in the second chamber to modify the surface of the article;

(5) wherein the converted  $F_2$  gas is used before the fluoro compound excited in the first chamber is partially or wholly contacted with the surface of the article in the second chamber.

[0121] [G] The surface modification process of [D] or [E] wherein a vacuum pump is provided in the gas channel connecting the first chamber and the second chamber and said vacuum pump is used during the step of transporting the excited fluoro compound-containing gas from the first chamber to the second chamber.

[0122] [H] The surface modification process of any one of [A]-[G] further comprising the step of introducing an

inert gas and/or oxygen after conferring energy on the fluoro compound-containing gas before contacting the gas with the article to be surface-modified.

[0123] [I] The surface modification process of any one of [A]-[H] wherein the energy conferring step comprises ionizing the fluoro compound-containing gas.

[0124] [J] The surface modification process of any one of [A]-[I] wherein the fluoro compound is a gaseous fluoro compound selected from linear, branched or cyclic saturated perfluorocarbons, linear, branched or cyclic unsaturated perfluorocarbons, carbonyl fluorides, perfluoro hypofluorides, perfluoro peroxides, perfluoroether compounds, oxygen-containing fluorides, interhalogen fluorides, iodine-containing fluorides, sulfur-containing fluorides, nitrogen-containing fluorides, silicon-containing fluorides, rare gas-containing fluorides, or combinations thereof.

[0125] [K] The surface modification process of any one of [A]-[I] wherein the fluoro compound is selected from  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_{10}$ ,  $\text{C}_5\text{F}_{12}$ ,  $\text{C}_6\text{F}_{14}$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_3\text{F}_6$ ,  $\text{C}_4\text{F}_8$ ,  $\text{C}_5\text{F}_{10}$ ,  $\text{C}_6\text{F}_{12}$ ,  $\text{C}_4\text{F}_6$ ,  $\text{FCOF}$ ,  $\text{CF}_3\text{COF}$ ,  $\text{CF}_2(\text{COF})_2$ ,  $\text{C}_3\text{F}_7\text{COF}$ ,  $\text{CF}_3\text{OF}$ ,  $\text{C}_2\text{F}_5\text{OF}$ ,  $\text{CF}_2(\text{OF})_2$ ,  $\text{CF}_3\text{COOF}$ ,  $\text{CF}_3\text{OOCF}_3$ ,  $\text{CF}_3\text{COOOF}$ ,  $\text{CF}_3\text{OCF}_3$ ,  $\text{C}_2\text{F}_5\text{OC}_2\text{F}_5$ ,  $\text{C}_2\text{F}_4\text{OC}_2\text{F}_4$ ,  $\text{OF}_2$ ,  $\text{SOF}_2$ ,  $\text{SOF}_4$ ,  $\text{NOF}$ ,  $\text{ClF}_3$ ,  $\text{IF}_5$ ,  $\text{BrF}_5$ ,  $\text{BrF}_3$ ,  $\text{CF}_3\text{I}$ ,  $\text{C}_2\text{F}_5\text{I}$ ,  $\text{N}_2\text{F}_4$ ,  $\text{NF}_3$ ,  $\text{NOF}_3$ ,  $\text{SiF}_4$ ,  $\text{Si}_2\text{F}_6$ ,  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{KrF}_2$ ,  $\text{SF}_4$ ,  $\text{SF}_6$ , or a mixture thereof.

[0126] [L] The surface modification process of any one of [A]-[K] wherein the fluoro compound-containing gas comprises an inert gas and/or oxygen.

[0127] [M] The surface modification process of [L] wherein the inert gas is He, Ne, Ar, Xe, Kr, N<sub>2</sub>, or a combination thereof.

[0128] [N] The surface modification process of any one of [A]-[M] wherein the fluoro compound is one or more members selected from the group consisting of NF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, and COF<sub>2</sub>.

[0129] [O] The surface modification process of [N] wherein the fluoro compound is ionized in the presence of oxygen when it is a perfluorocarbon or a mixture containing one or more perfluorocarbons.

[0130] [P] The surface modification process of any one of [A]-[O] wherein the surface modification is performed by fluorinating the surface of the article.

[0131] [Q] The surface modification process of any one of [A]-[P] wherein the article to be surface-modified is a metal and/or metal compound and/or polymer.

[0132] [R] The surface modification process of [Q] wherein the polymer is an article based on polypropylene.

[0133] [S] The surface modification process of [Q] wherein the metal compound is one or more members selected from the group consisting of metal oxides, metal nitrides, metal carbides, metal hydroxides and metal chlorides.

[0134] [T] The surface modification process of [Q] wherein the metal compound is a compound based on Si, especially Si, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiC, polysilicon, amorphous silicon, or a combination thereof.

[0135] [U] The surface modification process of [T]

wherein the compound based on Si is deposited in an LPCVD equipment.

[0136] [V] A surface modification equipment comprising:

a first zone including a means for ionizing a fluoro compound-containing gas under reduced pressure, and

a second zone communicating with the first zone and including an article to be surface-modified therein and a means for contacting a fluorine-containing gas generated by controlling the pressure under normal pressure or overpressure with the surface of the article under reduced pressure or overpressure to modify the surface of the article.

[0137] [W] A surface modification equipment comprising:

a first chamber including a means for ionizing a fluoro compound-containing gas under reduced pressure, and

a second chamber communicating with the first chamber and including an article to be surface-modified therein and a means for contacting a fluorine-containing gas generated by controlling the pressure under normal pressure or overpressure with the surface of the article under reduced pressure or overpressure to modify the surface of the article.

[0138] [X] The surface modification equipment of [W] wherein a vacuum pump or compressor is provided before and/or after the second chamber.

[0139] [Y] The surface modification equipment of [X] wherein the first chamber, second chamber, and vacuum pump are successively connected and the first chamber and second

chamber are independently connected with the vacuum pump or the surface modification equipment of [X] wherein the first chamber, compressor, and second chamber are successively connected and the first chamber and compressor are independently connected with the second chamber.

[0140] [Z] A method for using the equipment of [V]-[Y] to directly fluorinate an organic and/or inorganic material.

CLAIMS

[1] A process for preparing an F<sub>2</sub>-containing gas comprising the steps of:

exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas under reduced pressure; and

partially or completely converting the excited fluoro compound-containing gas containing the excited fluoro compound into F<sub>2</sub> under normal pressure or overpressure.

[2] The process for preparing an F<sub>2</sub>-containing gas of claim 1 wherein the step of exciting a fluoro compound is performed in a first zone maintained under reduced pressure; and

the step of converting the gas into F<sub>2</sub> is performed in a second zone communicating with the first zone and maintained under normal pressure or overpressure.

[3] The process for preparing an F<sub>2</sub>-containing gas of claim 1 wherein the step of exciting a fluoro compound is performed in a first zone maintained under reduced pressure; and

the step of converting the gas into F<sub>2</sub> comprises maintaining the pressure in the transportation system under a normal pressure or overpressure condition during transportation of the excited fluoro compound-containing gas to a second zone communicating with the first zone.

[4] The process for preparing an F<sub>2</sub>-containing gas of claim 1 wherein the step of exciting a fluoro compound is



performed in a first zone maintained under reduced pressure; and

the step of converting the gas into  $F_2$  is performed by maintaining the pressure in the first zone under a normal pressure or overpressure condition.

[5] The process for preparing an  $F_2$ -containing gas of claim 1 wherein the step of exciting a fluoro compound is performed in a first chamber maintained under reduced pressure; and

the step of converting the gas into  $F_2$  comprises transporting the excited fluoro compound-containing gas containing the excited fluoro compound from the first chamber to a second chamber maintained under normal pressure or overpressure via a gas channel connecting the first chamber and the second chamber.

[6] The process for preparing an  $F_2$ -containing gas of claim 1 wherein the step of exciting a fluoro compound is performed in a first chamber maintained under reduced pressure; and

the step of converting the gas into  $F_2$  comprises maintaining the pressure in the transportation system under a normal pressure or overpressure condition during transportation of the excited fluoro compound-containing gas containing the excited fluoro compound from the first chamber to a second chamber via a gas channel connecting the first chamber and the second chamber.

[7] The process for preparing an  $F_2$ -containing gas of claim 1 wherein the step of exciting a fluoro compound is

performed in a first chamber maintained under reduced pressure; and

the step of converting the gas into  $F_2$  is performed in the first chamber by maintaining the first chamber under normal pressure or overpressure.

[8] The process for preparing an  $F_2$ -containing gas of claim 5 or 6 wherein a vacuum pump is provided in a gas channel connecting the first chamber and the second chamber and said vacuum pump is used during the step of transporting the excited fluoro compound-containing gas from the first chamber to the second chamber.

[9] The process for preparing an  $F_2$ -containing gas of any one of claims 1 to 8 wherein the step of exciting a fluoro compound comprises ionizing the fluoro compound-containing gas.

[10] The process for preparing an  $F_2$ -containing gas of any one of claims 1 to 9 wherein the fluoro compound is a gaseous fluoro compound selected from linear, branched or cyclic saturated perfluorocarbons, linear, branched or cyclic unsaturated perfluorocarbons, carbonyl fluorides, perfluoro hypofluorides, perfluoro peroxides, perfluoroether compounds, oxygen-containing fluorides, interhalogen fluorides, iodine-containing fluorides, sulfur-containing fluorides, nitrogen-containing fluorides, silicon-containing fluorides, rare gas-containing fluorides, or combinations thereof.

[11] The process for preparing an  $F_2$ -containing gas of any one of claims 1 to 9 wherein the fluoro compound is

selected from  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_{10}$ ,  $\text{C}_5\text{F}_{12}$ ,  $\text{C}_6\text{F}_{14}$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_3\text{F}_6$ ,  $\text{C}_4\text{F}_8$ ,  $\text{C}_5\text{F}_{10}$ ,  $\text{C}_6\text{F}_{12}$ ,  $\text{C}_4\text{F}_6$ ,  $\text{FCOF}$ ,  $\text{CF}_3\text{COF}$ ,  $\text{CF}_2(\text{COF})_2$ ,  $\text{C}_3\text{F}_7\text{COF}$ ,  $\text{CF}_3\text{OF}$ ,  $\text{C}_2\text{F}_5\text{OF}$ ,  $\text{CF}_2(\text{OF})_2$ ,  $\text{CF}_3\text{COOF}$ ,  $\text{CF}_3\text{OOCF}_3$ ,  $\text{CF}_3\text{COOOF}$ ,  $\text{CF}_3\text{OCF}_3$ ,  $\text{C}_2\text{F}_5\text{OC}_2\text{F}_5$ ,  $\text{C}_2\text{F}_4\text{OC}_2\text{F}_4$ ,  $\text{OF}_2$ ,  $\text{SOF}_2$ ,  $\text{SOF}_4$ ,  $\text{NOF}$ ,  $\text{ClF}_3$ ,  $\text{IF}_5$ ,  $\text{BrF}_5$ ,  $\text{BrF}_3$ ,  $\text{CF}_3\text{I}$ ,  $\text{C}_2\text{F}_5\text{I}$ ,  $\text{N}_2\text{F}_4$ ,  $\text{NF}_3$ ,  $\text{NOF}_3$ ,  $\text{SiF}_4$ ,  $\text{Si}_2\text{F}_6$ ,  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{KrF}_2$ ,  $\text{SF}_4$ ,  $\text{SF}_6$ , or a mixture thereof.

[12] The process for preparing an  $\text{F}_2$ -containing gas of any one of claims 1 to 11 wherein the fluoro compound-containing gas comprises an inert gas and/or oxygen.

[13] The process for preparing an  $\text{F}_2$ -containing gas of claim 12 wherein the inert gas is He, Ne, Ar, Xe, Kr,  $\text{N}_2$ , or a combination thereof.

[14] The process for preparing an  $\text{F}_2$ -containing gas of any one of claims 1 to 13 wherein the fluoro compound is one or more members selected from the group consisting of  $\text{NF}_3$ ,  $\text{C}_2\text{F}_6$ , and  $\text{COF}_2$ .

[15] The process for preparing an  $\text{F}_2$ -containing gas of claim 14 wherein the fluoro compound is ionized in the presence of oxygen when it is a perfluorocarbon or a mixture containing one or more perfluorocarbons.

[16] A process for modifying the surface of an article comprising contacting an  $\text{F}_2$ -containing gas obtained by the process for preparing an  $\text{F}_2$ -containing gas of any one of claims 1 to 15 with the surface of the article under reduced pressure or overpressure or normal pressure.

[17] The surface modification process of claim 16 further comprising the step of introducing an inert gas and/or oxygen after conferring energy on the fluoro

compound-containing gas before contacting the gas with the article to be surface-modified.

[18] The surface modification process of claim 16 or 17 wherein the surface modification is performed by fluorinating the surface of the article.

[19] The surface modification process of any one of claims 16 to 18 wherein the article to be surface-modified is one or more members selected from the group consisting of metals, metal compounds and polymers.

[20] The surface modification process of claim 19 wherein the polymer is an article based on polypropylene.

[21] The surface modification process of claim 19 wherein the metal compound is one or more members selected from the group consisting of metal oxides, metal nitrides, metal carbides, metal hydroxides and metal chlorides.

[22] The surface modification process of claim 19 wherein the metal compound is a compound based on Si.

[23] The surface modification process of claim 22 wherein the compound based on Si is Si, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiC, polysilicon, amorphous silicon, or a combination thereof.

[24] The surface modification process of claim 22 wherein the compound based on Si is deposited in an LPCVD equipment.

[25] An equipment for preparing an F<sub>2</sub>-containing gas comprising:

a means for ionizing a fluoro compound-containing gas under reduced pressure; and

a pressure controlling means communicating with the

ionizing means and controlling the pressure of the ionized fluoro compound-containing gas at a normal pressure or overpressure condition.

[26] A surface modification equipment comprising a means communicating with the pressure controlling means in the equipment for preparing an F<sub>2</sub>-containing gas of claim 25 and positioning an article whose surface should be contacted with the F<sub>2</sub>-containing gas prepared in the equipment for preparing an F<sub>2</sub>-containing gas under reduced pressure or overpressure or normal pressure.

[27] The surface modification equipment of claim 26 further comprising a vacuum pump or compressor communicating with the means for positioning the article.

[28] A method for using the equipment of any one of claims 25 to 27 to directly fluorinate an organic and/or inorganic material.

# ABSTRACT

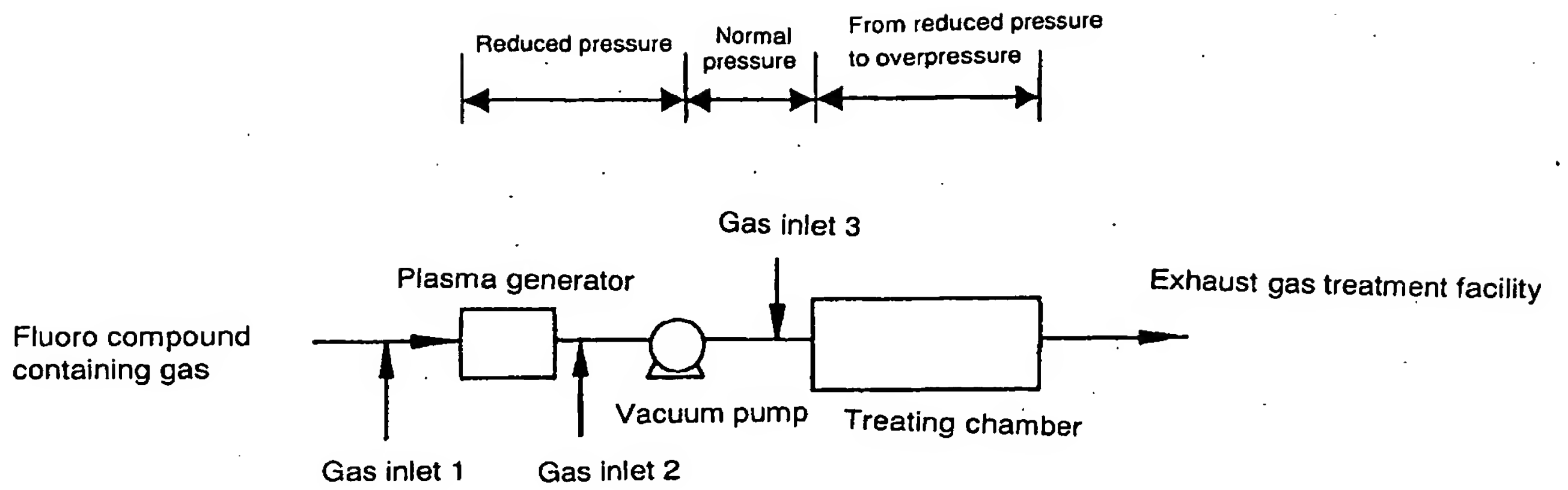
The present invention provides processes and equipments for safely and easily preparing an  $F_2$ -containing gas, as well as processes and equipments for surface modification using the  $F_2$ -containing gas prepared.

According to the present invention, a gas containing a fluoro compound that is easier to handle than  $F_2$  is supplied and the fluoro compound is excited and decomposed to convert it into  $F_2$  gas before surface modification and then used for surface modification. According to the present invention, there is no necessity of providing, storing and transporting a large amount of  $F_2$  gas in advance because a necessary amount of  $F_2$  gas is obtained immediately before surface modification.

A process for preparing an  $F_2$ -containing gas comprises the steps of exciting at least one fluoro compound in a fluoro compound-containing gas by conferring energy on the fluoro compound-containing gas under reduced pressure; and partially or completely converting the excited fluoro compound-containing gas containing the excited fluoro compound into  $F_2$  under normal pressure or overpressure.



Figure 1





**Erfindernennung**  
**Designation of inventor**  
**Désignation de l'inventeur**

(falls Anmelder nicht oder nicht allein der Erfinder ist) /  
(where the applicant is not the inventor or is not the  
sole inventor) / (si le demandeur n'est pas l'inventeur  
ou l'unique inventeur)

<b>Zeichen des Anmelders oder Vertreters:</b> Applicant's or representative's reference: Référence du demandeur ou du mandataire : (max. 15 Positionen / max. 15 spaces / 15 caractères au maximum)	<b>Nr. der Anmeldung oder, falls noch nicht bekannt, Bezeichnung der Erfindung:</b> Application No. or, if not yet known, title of the invention : N° de la demande ou, s'il n'est pas encore connu, titre de l'invention:
069EP 1009 SE	05 727 964.8 – WO 2005/095268  PROCESSES AND EQUIPMENTS FOR PREPARING F2-CONTAINING GASES, AS WELL AS PROCESSES AND EQUIPMENTS FOR MODIFYING THE SURFACES OF ARTICLES

In Sachen der obenbezeichneten europäischen Patentanmeldung nennt (nennen) der (die) Unterzeichnete(n)<sup>1</sup>  
In respect of the above European patent application I (we), the undersigned<sup>1</sup>  
En ce qui concerne la demande de brevet européen susmentionnée, le(s) soussigné(s)<sup>1</sup>

**Dr. H. Gleiter – Patent Attorney**

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☐ Weitere Erfinder sind auf einem gesonderten Blatt angegeben. / Additional inventors indicated on supplementary sheet. /  
D' autres inventeurs sont mentionnés sur une feuille supplémentaire.

Der (Die) Anmelder hat (haben) das Recht auf das europäische Patent erlangt<sup>3</sup>  
The applicant(s) has (have) acquired the right to the European patent<sup>3</sup>  
Le(s) demandeur(s) a (ont) acquis le droit au brevet européen<sup>3</sup>

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Ort/Place/Lieu : Munich, Datum/Date : July 10, 2006

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than semiconductors such as metal materials and plastic materials using a plasma derived from a fluoro compound have been reported (see patent document <sup>3</sup>~~2~~, and patent document 4). However, the plasma may penetrate into the article to be surface-treated to damage the article in these methods.

[0005] A surface treatment method using unionized F<sub>2</sub> gas has also been reported (e.g., see patent document <sup>2</sup>~~2~~).

However, the method directly using F<sub>2</sub> gas has the following problems. First, it is difficult to store, transport and use a large amount of F<sub>2</sub> gas because of the toxicity, hazardousness, reactivity, and corrosiveness of F<sub>2</sub> gas. In order to reduce hazardousness, diluted F<sub>2</sub> gas can be used, but costs for storage and transportation increase.

Moreover, very stable materials must be used for the sites exposed to F<sub>2</sub> gas, which add costs of the surface treatment equipment.

[0006] A method for treating the surface of an article comprising exciting a halogen compound by applying a low-frequency voltage on it at or near atmospheric pressure to decompose it and generate a halogen or hydrogen halide has also been proposed (see patent document 5). This method has the advantage that it is simple and safe to operate because it can be performed at or near atmospheric pressure. However, the concentration of the halogen or hydrogen halide that can be generated by this method is considerably low because of low decomposition efficiency and it is not easy to secure a sufficient concentration or amount for the

# Empfangsbescheinigung / Receipt for documents / Récépissé de documents 6

(Liste der diesem Antrag beigefügten Unterlagen)

(Checklist of enclosed documents)

(Liste des documents annexés à la présente requête)

Es wird hiermit der Empfang der unten bezeichneten Dokumente bescheinigt / Receipt of the documents indicated below is hereby acknowledged / Nous attestons le dépôt des documents désignés ci-dessous

Wird im Falle der Einreichung der europäischen Patentanmeldung bei einer nationalen Behörde diese Empfangsbescheinigung vom Europäischen Patentamt übersandt, so ist sie als Mitteilung gemäß Regel 24(4) anzusehen (siehe Feld RENA). Nach Erhalt der Mitteilung nach Regel 24(4) sind alle weiteren Unterlagen, die die Anmeldung betreffen, nur noch unmittelbar beim EPA einzureichen. / If this receipt is issued by the European Patent Office and the European patent application was filed with a national authority it serves as a communication under Rule 24(4) (see Section RENA). Once the communication under Rule 24(4) has been received, all further documents relating to the application must be sent directly to the European Patent Office. / Si, en cas de dépôt de la demande de brevet européen auprès d'un service national, l'Office européen des brevets délivre le présent récépissé de documents, ce récépissé est réputé être la notification visée à la règle 24(4) (cf. rubrique RENA). Dès que la notification visée à la règle 24(4) a été reçue, tous les autres documents relatifs à la demande doivent être adressés directement à l'OEB.

PFENNING, MEINIG & PARTNER GbR

Patentanwälte

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Anmeldenummer / Application No. / N° de la demande		05 727 964.8	
Tag des Eingangs (Regel 24(2)) / Date of receipt (Rule 24(2)) / Date de réception (règle 24(2))	DREC		
Zeichen des Anmelders/Vertreters / Applicant's/ Representative's ref. / Référence du demandeur ou du mandataire	AREF	069EP 1009 SE	
Nur nach Einreichung der Anmeldung bei einer nationalen Behörde: / Only after filing of the application with a national authority: / Seulement après le dépôt de la demande auprès d'un service national:			
Tag des Eingangs beim EPA (Regel 24(4)) / Date of receipt at EPO (Rule 24(4)) / Date de réception à l'OEB (règle 24(4))	RENA		
<b>A. Anmeldeunterlagen und Prioritätsbeleg(e) / Application documents and priority document(s) / Pièces de la demande et document(s) de priorité</b> 1. Beschreibung (ohne Sequenzprotokollteil) / Description (excluding sequence listing part) / Description (sauf partie réservée au listage des séquences) 2. Patentansprüche / Claim(s) / Revendication(s) 3. Zeichnung(en) / Drawing(s) / Dessin(s) <b>DRAW 1 #</b> 4. Sequenzprotokollteil der Beschreibung / Sequence listing part of description / Partie de la description réservée au listage des séquences 5. Zusammenfassung / Abstract / Abrégé 6. Übersetzung der Anmeldeunterlagen / Translation of the application documents / Traduction des pièces de la demande 7. Prioritätsbeleg(e) / Priority document(s) / Document(s) de priorité 8. Übersetzung des (der) Prioritätsbelegs(belege) / Translation of priority document(s) / Traduction du (des) document(s) de priorité		47	Blattzahl* / Number of sheets* / Nombre de feuilles* Gesamtzahl der Abbildungen* / Total number of figures* / Nombre total de figures* <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input checked="" type="checkbox"/>
<b>B. Der Anmeldung in der eingereichten Fassung liegen folgende Unterlagen bei: / This application as filed is accompanied by the items below: / A la présente demande sont annexées les pièces suivantes:</b> 1. Einzelvollmacht / Specific authorisation / Pouvoir particulier 2. Allgemeine Vollmacht / General authorisation / Pouvoir général 3. Erfindernennung / Designation of inventor / Désignation de l'inventeur 4. Früherer Recherchenbericht / Earlier search report / Rapport de recherche antérieure 5. Gebührenzahlungsvordruck (EPA Form 1010) / Voucher for the settlement of fees (EPO Form 1010) / Bordereau de règlement de taxes (OEB Form 1010) 6. Scheck (nicht bei Einreichung bei den nationalen Behörden) / Cheque (not when filing with national authorities) / Chèque (pas de chèque en cas de dépôt auprès des services nationaux) 7. Datenträger für Sequenzprotokoll / Data carrier for sequence listing / Support de données pour liste de séquences <b>SEQL 4</b> 8. Zusatzblatt / Additional sheet / Feuille additionnelle 9. Sonstige Unterlagen (bitte hier spezifizieren) / Other documents (please specify here) / Autres documents (veuillez préciser) <b>C. Kopien dieser Empfangsbescheinigung / Copies of this receipt for documents / Copies du présent récépissé de documents</b>		48	* Die Richtigkeit der Angabe der Blattzahl und der Gesamtzahl der Abbildungen wurde bei Eingang nicht geprüft / No check was made on receipt that the number of sheets and the total number of figures indicated were correct / L'exactitude du nombre de feuilles et du nombre total de figures n'a pas été contrôlée lors du dépôt Währung Betrag / Currency Amount / Monnaie Montant (Ausfüllung freigestellt / optional / facultatif) <b>EUR 3.711,00</b> <input checked="" type="checkbox"/> Amended description page 2
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